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Preface

The work presented in this PhD thesis was carried out at the Department of Environmental Engineering of the Technical University of Denmark under the supervision of Professor Thomas F. Astrup, from September 2013 to September 2017. The work included a three months stay, from January 2016 to April 2016, at the Bundesanstalt für Materialforschung und -prüfung (BAM, Germany) and collaborations with Danish Waste Solutions ApS and the Department of Geosciences and Natural Resource Management of the University of Copenhagen.

The thesis is organised in two parts, the first of which provides background information and places the findings of the PhD into context, while the second part consists of the papers listed below. These will be referred to in the text by their paper number, denoted by the Roman numerals **I-IV**.

I Maresca, A., Jyks, J., Astrup, T.F. (2017). Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties. Waste Management. *Accepted.* [Paper **I**]

II Maresca, A., Jyks, J., Astrup, T.F. (2017). Long-term leaching of nutrients and contaminants from wood combustion ashes. *Submitted.* [Paper **II**]

III Maresca, A., Hansen, M., Ingerslev, M., Astrup, T.F. (2017). Recirculation of wood combustion ashes onto Danish forest soil: release of nutrients and heavy metals. *Submitted.* [Paper **III**]

IV Maresca, A., Kruger, O., Herzel, H., Adam, C., Kalbe, U., Astrup T.F. (2017). Influence of wood ash pre-treatment on leaching behaviour, liming and fertiliser potential. *Manuscript.* [Paper **IV**]

This PhD work is part of the ASHBACK project (http://ashback.dk/), financed by The Danish Council for Strategic Research. The ASHBACK project aims to investigate the amounts of wood ash that can be applied onto forest soils without significant consequences for the environment and human health.

In addition, the following publications, not included in this thesis, were also concluded during this PhD study:

- Maresca, A. and Astrup, T.F. (2014). Leaching from biomass combustion ash. *Proceedings Venice 2014, Fifth International Symposium on Energy from Biomass and Waste. San Servolo, Venice, Italy; 17 - 20 November 2014.*
- Maresca, A. and Astrup, T.F. (2015). Column leaching from biomass combustion ashes. *Proceedings Sardinia 2015, Fifteenth International Waste Management and Landfill Symposium. S. Margherita di Pula, Cagliari, Italy; 5 – 9 October 2015.*

TEXT FOR WWW-VERSION (without papers)

In this online version of the thesis, paper **I-IV** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Bygningstorvet, Building 115, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

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My *mum, dad, little sister* and *grandparents* are acknowledged for their continuous love and support. Last but not least, my gratitude goes to *Carlita* for her patience, love, encouragement and for being a daily part of my family here.

Summary

The combustion of wood chips and wood pellets for the production of renewable energy in Denmark increased from 5.7 PJ to 16 PJ during the period 2000-2015, and further increases are expected to occur within the coming years. In 2012, about 22,300 tonnes of wood ashes were generated in Denmark. Currently, these ashes are mainly landfilled, despite Danish legislation allowing their application onto forest and agricultural soils for fertilising and/or liming purposes.

During this PhD work, 16 wood ash samples generated at ten different Danish combustion plants were collected and characterised for their composition and leaching properties. Despite the relatively large variations in the contents of nutrients and trace metals, the overall levels were comparable to typical ranges reported in the literature for other wood combustion ashes, as well as with regards to leaching. In general, the composition of the ashes complied with Danish ash quality criteria, indicating that they may be applied onto forest soil. However, according to EU landfill waste acceptance criteria, the leachates corresponded to “non-hazardous” or “hazardous” waste, thereby suggesting that recirculation of the same ashes to forestry land may constitute an environmental issue as a result of leaching, especially with regards to Cr and Se.

The release of nutrients and contaminants from two selected wood ash samples (corresponding to one mixed ash sample and one fly ash sample) was estimated based on selected pH conditions and data for both short- and long-term leaching. Acidic conditions relevant for typical forest soils in Denmark indicated considerably higher releases of Cd, Mg, Zn and P compared with releases of the natural ash pH (more than two orders of magnitude difference). The leaching of Cl, K, Na and S was rather pH-independent, high during the initial leaching and most likely governed by the availability of these elements in the ash matrix. On the other hand, the leaching of Al, Ba, Ca, Cr, Mg, Sb, V and Zn was distributed over a wider liquid-to-solid (L/S) interval and differences of at least one order of magnitude were shown between the observed cumulative releases at L/S 10 L/kg and L/S 1000 L/kg. Relatively large fractions of P (i.e. 33 % and 48 % of the fly ash and mixed ash P contents, respectively) were observed to dissolve after extraction with neutral ammonium citrate, which indicated the potential use of wood ashes as a P supplement for the soil.

The release of major elements such as Al, Ba, Ca, Fe, Mg, Si, P and S was governed mainly by mineral solubility. The most likely minerals governing the release of these elements were found to be in general agreement with mineral phases identified in the literature for other wood combustion ashes, but also municipal solid waste incineration ashes. The leaching of trace elements, such as Cu, Cr, Pb and Zn, was described adequately as a combination of mineral solubility, adsorption onto Al/Fe (hydr-) oxides and complexation with dissolved organic matter.

The influence of common ash pre-treatments, such as hardening (also known as ageing or maturing) and granulation, on ash chemistry, liming potential and leaching behaviour was investigated through a series of laboratory experiments. Ash granules were relatively hard (barely breakable by finger-pinching) and demonstrated a reduced leaching compared to loose ashes, an effect that appeared to be related to the specific surface area granules. Ash granules may be used in actual field applications to minimise dust generation. Hardening affected the mineralogical structure of the ashes, but their overall acid neutralisation capacity remained practically constant. Column leaching tests showed that hardened ashes presented pH levels about two units lower than fresh ashes and a reduced leaching of alkalinity. The leaching of As, P, Sb and V increased after hardening, while the leaching of Ba, Ca, Pb and Zn was generally reduced to concentration levels below or close to limit of quantitation levels. Ash hardening was observed to be a relatively simple and fast treatment. Preferably, this process should be carried out under controlled conditions, before the ashes are applied, as this will minimise their overall reactivity as well as the leaching of most trace elements.

The effects of ash application on the mobility of nutrients and trace elements in soil pore water were evaluated through a series of column experiments. The two uppermost soil horizons of a Danish nutrient-poor forest soil were tested against three ash dosages, namely 3, 9 and 30 tonnes/ha. Ash application promoted the release of nutrients such as K and P during the entire duration of the experiment, corresponding to about eight field-scale years. A short-term release of Cl, K, Mg and S was also observed within the first 500 L/m^2 of infiltrating water (corresponding to fewer than two years on the field scale). While an overall increase in the leached amounts of As and Cu from the organic soil horizon were observed in the case of ash application (from 2.2 to 5.0-5.8 mg/m^2 for As and from 2.0 to 4.9-7.6 mg/m^2 for Cu), their concentration levels in the percolating soil solutions was generally

within Danish groundwater quality criteria. Though the effects of both the 3 and 9 tonnes/ha dosages were limited and comparable, the use of 30 tonnes/ha indicated considerably larger amounts of K, Mg, S and Si within the first 500 L/m^2 (at least five times larger than the soil controls). Furthermore, because of the low mobility of many trace elements, such as Cd, Cr, Ni, Pb and Zn, potential accumulation of these elements on the forest floor should be evaluated. Consequently, such high dosages cannot be recommended based on these experiments.

Dansk sammenfatning

Produktion af vedvarende energi fra forbrænding af træflis og træpiller er i Danmark steget fra 5,7 PJ til 16 PJ i perioden 2000-2015 og yderligere stigninger forventes i de kommende år. I 2012 blev der i Danmark genereret omkring 22.300 tons træaske. I dag bliver størstedelen af asken deponeret, til trods for at den danske lovgivning muliggør anvendelse af træasken til jordbrugsformål som gødning og/eller som erstatning for kalk i skovene og i landbruget.

Den kemiske sammensætning og udvaskningsegenskaberne af 16 forskellige træasker indsamlet fra ti danske fjernvarmeanlæg blev undersøgt. På trods af den relativt store variation i indholdet af næringsstoffer og spormetaller var de overordnede niveauer sammenlignelige med typiske data i litteraturen for andre asker fra forbrænding af træ, også i relation til udvaskning. Generelt opfyldte træaskerne de danske kvalitetskriterier, hvilket indikerer, at askerne kan anvendes til jordforbedring i skovene. Tages der i stedet udgangspunkt i EU's modtagelseskriterier for affald til deponering svarer udvaskningen fra træaskerne til en klassificering som enten ”ikke-farligt affald” eller ”farligt affald”. Dette indikerer, at genanvendelsen af asken i skovbrug kan udgøre et potentielt miljøproblem, særligt i forhold til udvaskning af Cr og Se.

Udvaskning af næringsstoffer og forureningselementer fra to udvalgte asker (én blandet aske bestående af bund- og flyveaske, samt én flyveaske) blev undersøgt ved forskellige pH-niveauer såvel som i forhold til den kort- og langsigtede udvaskning via kolonneforsøg. Sure jordbundsforhold typisk for danske skove resulterede i væsentlig højere udvaskning af Cd, Mg, Zn and P sammenlignet med udvaskningen ved askernes naturlige pH-forhold (mere end to størrelsesordner højere). Udvaskningen af Cl, K, Na og S var relativ uafhængig af pH, høj i starten af udvaskningsperioden, og sandsynligvis styret af tilgængeligheden af disse elementer i askematricen. Udvaskningen af Ca, Cr, Mg, Sb, V og Zn var derimod fordelt over en længere periode (og et højere liquid-to-solid, L/S, forhold) med forskelle på mindst én størrelsesorden mellem den akkumulerede udvaskning ved L/S 10 L/kg og L/S 1000 L/kg. Relativt store P-mængder (33-48 % af indholdet i de to asketyper) kunne opløses ved ekstraktion med ammoniumcitrat, hvilket indikerer, at træaskerne har potentiale som P-supplement til jorden.

Udvaskningen af elementer som Al, Ba, Ca, Fe, Mg, Si, P and S var styret primært af askemineralernes opløselighed. De identificerede mineraler

svarede til tilsvarende mineralfaser fundet i litteraturen for andre træasker, såvel som for asker fra forbrænding af affald. Udvaskningen af sporstoffer som Cu, Cr, Pb og Zn kunne beskrives ved en kombination af mineralernes opløselighed, adsorption til Al/Fe (hydr-) oxider og kompleksbinding til opløst organisk stof.

En række forbehandlingsmetoder, nemlig hærdning (også kendt som modning) og granulering, blev undersøgt i forhold til ændringer i askernes kemiske sammensætning og udvaskningsegenskaber. Granulering af askerne dannede relativt hårde partikler og medførte en reduceret udvaskning sammenlignet med aske i løs form; en effekt som formentlig skyldes ændringen i specifikt overfladeareal. Granulering af asken vil reducere støvdannelsen ved udspredning til jordbrugsformål. Hærdning påvirkede askens mineralstruktur, mens askernes samlede bufferkapacitet (alkalinitet) i praksis forblev uændret. Udvaskning fra kolonneforsøg viste, at den hærdede aske havde et pH-niveau omkring to enheder lavere end for den friske aske samt en lavere udvaskning af alkalinitet. Udvaskningen af As, P, Sb and V var højere efter hærdning, mens udvaskningen af Ba, Ca, Pb, og Zn var reduceret til koncentrationer tæt på eller under detektionsgrænsen. Hærdning af askerne blev vurderet som en relativ simple og hurtig forbehandlingsproces. Det anbefales, at hærdningen gennemføres under kontrollerede forhold før udspredning af askerne, da hærdningen vil kunne mindske askernes reaktivitet og den samlede udvaskning.

Påvirkningen af nærings- og spormetallernes mobilitet via porevandet i jorden blev undersøgt i en række kolonneforsøg med både aske og jord. De øverste to jordlag fra en dansk næringsfattig skovbund blev undersøgt med tilsætning af tre forskellige askeniveauer: 3, 9 og 30 tons/ha. Asketilførslen øgede frigivelsen af næringsstoffer som K og P igennem hele eksperimentet svarende til udvaskning over ca. otte år i felten. En øget udvaskning af Cl, K, Mg, og S blev observeret inden for en infiltration svarende til de første 500 L/m^2 (svarende til mindre end to år). Selvom en stigning i den udvaskede mængde af As og Cu blev observeret fra kolonnerne (fra 2,2 til 5,0-5,8 mg/m^2 for As og 2,0 til 4,9-7,6 mg/m^2 for Cu) var koncentrationsniveauerne generelt i overensstemmelse med de danske grundvandskvalitetskriterier. Effekterne fra 3 og 9 tons/ha var begrænsede og sammenlignelige, mens tilførslen af 30 tons/ha indikerede væsentlig højere udvaskning af K, Mg, S og Si inden for de første 500 L/m^2 (mere en fem gange større mængder end i kontrolforsøgene uden aske). Den lave mobilitet af spormetaller såsom Cd,

Cr, Ni, Pb og Zn indikerer dog, at potentialet for akkumulering af disse elementer i jorden bør undersøges nærmere. Baseret på resultaterne kan en høj tilførsel på 30 tons/ha ikke umiddelbart anbefales.

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Abbreviations

ACRONYMS

ANC	Acid Neutralisation Capacity
DEPA	Danish Environmental Protection Agency
L/S	Liquid-to-Solid
MSWI	Municipal solid waste incineration
PAH	Polycyclic aromatic hydrocarbon
XRD	X-ray diffraction

UNITS

ha	Hectare
PJ	Peta-joule (1 PJ $=10^{15}$ J)
y	Year

1 Introduction

1.1 Background

Increasing amounts of wood chips and wood pellets have been used in Denmark for the production of renewable energy over the last 15 years, i.e. from 5.7 PJ to 16 PJ during the period 2000-2015 (Danish Energy Agency, 2017), resulting in more wood ashes being generated. In general, depending on the specific wood type, about 0.4-1.8 % dry weight of ashes are produced during the combustion process (Skov and Ingerslev, 2013). In Denmark, although wood ashes may be applied onto forest soils, these materials have been mainly landfilled (Ingerslev et al., 2014), likely because of the relatively small amounts of wood ash generated at individual Danish heat and power plants, high costs associated with documenting ash quality and concerns about composition and leachability.

The utilisation of wood ashes on forest soils is regulated in Denmark (DEPA, 2008) in terms of maximum levels of contaminants (i.e. Cd, Hg, Pb, Ni, Cr and polycyclic aromatic hydrocarbons (PAHs)), electrical conductivity, dosages and application frequency. A maximum of 3 tonnes/ha/10y can be applied three times over a 75-year period, though the addition of Cd through the wood ashes should not exceed the limit of 60 g Cd/ha/75y. Nevertheless, depending on the ash electrical conductivity levels and on the soil fertilising needs, lower dosages may be required. With increasing amounts of wood ashes being generated, there is a general interest to recirculate these materials back to forest soils and to evaluate the possibility of higher application dosages. A thorough assessment of the ashes' chemical composition and leachability, and of the potential interactions between ashes and forest soil, is however needed in order to clarify the potential benefits and risks associated with this practice.

Depending on the type of wood, the combustion technology and the ash type (bottom ash, fly ash and mixed ash), the composition of wood ashes has been shown to vary considerably across individual samples (e.g. SLU, 2008). Overall, however, the relatively high levels of nutrients and acid neutralisation capacity make these waste materials a potentially valuable source of nutrients and alkalinity, which may be used to counteract acidification and nutrient depletion of forest soils (Swedish Forest Agency, 2008). On the other hand, the content of contaminants in the ash may raise concerns about soil quality, if released, which is also why only wood ashes from "clean biomass fuels" are generally allowed to be recirculated onto soil (van Eijk et al., 2012). A comprehensive

characterization of Danish wood ashes can provide a solid background to assess the potential for these ashes to be utilized.

Leaching tests can provide useful information on source-term releases from ashes in terms of nutrients and contaminants, releasing mechanisms and short-/long-term leaching. In the literature, the leaching properties of wood ashes have been investigated by means of different sequential extraction, batch and column methods (Liodakis et al., 2009; Mellbo et al., 2008; Pöykiö et al., 2012; Sano et al., 2013; Steenari et al., 1998a, 1999a; Supancic et al., 2014). However, while the use different operating conditions has helped address specific aspects of ash leaching, the relatively large variability in test conditions makes it difficult to compare the results of individual studies directly.

Speciation calculations can be used as a supporting tool to interpret leaching test results and to identify processes such as mineral dissolution/precipitation, complexation to dissolved organic matter and sorption onto Fe/Al (hydr-)oxides. Nevertheless, while the use of geochemical models has been employed widely in municipal solid waste incineration (MSWI) ashes (e.g. Astrup et al., 2006a; Hyks et al., 2009a; Meima and Comans, 1997; Polettini and Pomi, 2004), only a few studies have carried out a comprehensive modelling of wood ashes that included a relatively wide range of elements (Allegrini et al., 2011; van der Sloot and van Zomeren, 2010).

Wood ashes may be pre-treated before being applied, albeit this is not a requirement of current Danish legislation. Common pre-treatments include the so-called “hardening” (also known as maturing, ageing or curing) and the physical compaction of ashes, achieved, for example, by granulation or pelletising. During hardening, freshly generated ashes, which are thermodynamically unstable in ambient conditions, undergo a series of spontaneous chemical reactions when in contact with moisture and atmospheric carbon dioxide – see Steenari and Lindqvist (1997) for a detailed description of the types of reactions. Granulation and pelletising aim at generating larger particles to facilitate the handling of the ashes and to attempt reducing the rate of leaching compared with untreated loose wood ashes. Specific additives may be added during this process to adjust the content of nutrients and/or strength of the particles. Leaching from hardened and granulated/pelletised wood ashes have been investigated through a series of batch experiments (e.g. Holmberg et al., 2000; Mellbo et al., 2008; Sarenbo, 2009; Steenari and Lindqvist, 1997; Steenari et al., 1999a, 1999b; Supancic et al., 2014), and seldom through equilibrium-based column leaching tests (Gori et al., 2011; Mellbo et al., 2008). While the

leaching of major elements has been generally characterized, the leaching of trace elements has received considerably lower attention. There is a general need for additional studies clarifying the effects of wood ash hardening and granulation/pelletising on the leaching of nutrients and contaminants and on the ash liming potential.

1.2 Research objectives

The overall aim of this PhD project is to strengthen knowledge on wood ash composition, leaching, pre-treatments and soil application, with a specific focus on Danish conditions. The specific research objectives of this work are to:

1. Characterise variability in the composition and basic leaching behaviour of Danish wood ashes, to identify potential geochemical processes governing the release of nutrients and contaminants and to estimate their source-term release at different pH conditions [Paper I]
2. Characterise the long-term leaching behaviour of wood ashes, to evaluate potential leaching mechanisms and identify cumulative releases from the ashes in a long-term perspective [Paper II]
3. Investigate the effects of hardening and granulation on wood ash chemistry, liming potential and the leaching of nutrients and contaminants [Paper IV]
4. Investigate the potential effects of different wood ash dosages on the composition of percolating soil solutions on a Danish nutrient-poor forest plantation soil [Paper III]

The synopsis part of this PhD thesis is structured as follows.

Section 2 provides an overview of the sampling, handling and analysis of both the wood ash samples and the soil samples. The overall experimental set-up and geochemical model is presented, too.

Section 3 provides an overview of wood ash composition, presented in comparison with data from the literature and Danish ash quality criteria. The major effects of hardening and granulation on the ashes' chemical properties are described.

Section 4 summarises the main results related to leaching. Batch leaching data are compared to the literature and acceptance criteria for waste disposal. Results from pH-dependent tests and column tests are presented and accompanied by geochemical modelling results. The major effects of hardening and granulation on leaching from ashes are reported.

Section 5 describes the influence of different wood ash dosages on the composition of the percolating soil solutions in comparison with Danish groundwater quality criteria. Potential environmental concerns owing to the migration of contaminants through the soil and/or the accumulation of these compounds within the forest floor are discussed.

Section 6 provides the overall conclusions of this PhD work, while **Section 7** offers future perspectives.

2 Materials and Methods

2.1 Wood ash and soil samples

Freshly generated wood ash samples were collected from ten different wood-to-energy facilities in Denmark using wood chips as fuel, mainly from Norway spruce (*Picea abies*). Nine grate-fired combustion plants and one gasification plant were included. Depending on the technology configuration (i.e. on whether the generated bottom ashes and fly ashes were transported in two separate flows or in a combined single flow), bottom ashes, fly ashes or mixed ashes were sampled. A total of 16 samples were collected: three bottom ash, four fly ash and nine mixed ash samples. Table 1 reports the list of samples, together with selected characteristics of the individual combustion plants. Herning and Assens are the only combined heat-and-power plants, while the others generate heat only.

In typical field applications, wood ashes are commonly spread on top of the forest floor and they are not worked in further. To investigate the effects of wood ash application on the forest soil, the two topmost soil horizons (namely, O- and A-horizons) were taken from a nutrient-poor sandy soil in a 57-year-old Norway spruce plantation, NW Denmark (56° 16’ 39” N; 9° 5’ 7” E Lat/Lon, WGS84). The direct application of wood ash onto O-horizon and A-horizon was investigated through a series a column tests - see more details on the experimental set-up in Section 2.5. The forest field has a mean annual temperature of 8.4°C, precipitation of 850 L/m^2 (Wang, 2013) and net rainfall infiltration of about 270 L/m^2 (Hansen et al., 2017).

Table 1. Wood ash samples and combustion facilities: main characteristics. From Paper **I**.

Sample	Ash type	Combustion plant	Combustion technology	Use of wood chips period: 2014 – 2015 (tonnes of wood chips /year)
BA-1	Bottom	Ebeltoft (I)	Grate fired	11000
BA-2	Bottom	Ebeltoft (II)	Grate fired	9000
BA-3	Bottom	Herning	Grate fired	252000
FA-1	Fly	Ebeltoft (I)	Grate fired	18000
FA-2a	Fly	Ebeltoft (II)	Grate fired	11000
FA-2b	Fly	Ebeltoft (II)	Grate fired	9000
FA-3	Fly	Herning	Grate fired	252000
MA-4	Mixed	Trustrup	Grate fired	4500
MA-5	Mixed	Allingåbro	Grate fired	5000
MA-6	Mixed	Kjellerup	Grate fired	17000
MA-7	Mixed	Assens J	Grate fired	5500
MA-8	Mixed	Galten	Grate fired	14900
MA-9a	Mixed	Brande	Grate fired	8500
MA-9b	Mixed	Brande	Grate fired	8500
MA-9c	Mixed	Brande	Grate fired	8500
MA-10	Mixed	Harboør	Gasification	9000

2.2 Sample characterisation

The 16 wood ash samples presented in Table 1 were split, milled, acid-digested and analysed for their elemental composition – more details on the methodology in Paper **I**. Moisture content, nitrogen, total carbon and total organic carbon were also determined. The electrical conductivity of the ashes was analysed (batch test at the liquid-to-solid (L/S) ratio 5 L/kg) by one of the ASHBACK partners (see Preface).

The application of wood ash on Danish forest soil is regulated based on ash total contents and electrical conductivity values (quality criteria), which in turn determine the maximum application dosage (DEPA, 2008): up to 1, 2 or 3 tonnes/ha/10y – see Section 3.1 for more details. Based on these ash quality criteria, two wood ash samples were selected and used throughout this PhD study more extensively: sample MA-9c, complying with the most stringent limits that allow an application dosage of 3 tonnes/ha/10y; sample FA-2b, for which application dosage is restricted to 1 tonne/ha/10y (because of the relatively high electrical conductivity, i.e. ~3300 mS/m). Noteworthy that sample FA-2b was specifically selected because of its content of Cd (16 mg/kg), which was the highest within the herein investigated wood ash samples. The two selected samples, i.e. MA-9c and FA-2b, were additionally characterised for their content of Hg, PAHs and the presence of crystalline mineral phases.

Soil samples were dried at 50ºC and sieved to <2 mm and <4 mm for the A-horizon and O-horizon, respectively. These were then ground, acid-digested and analysed for their elemental composition. The contents of total carbon and nitrogen were also analysed.

2.3 Ash pre-treatments

Current Danish legislation on the application of wood ashes onto forest soil does not require specific ash pre-treatments (DEPA, 2008), in contrast to the Swedish Forest Agency (2008) that recommends the use of "sufficiently hardened ash". In general, typical ash pre-treatments include hardening and physical compaction (Swedish Forest Agency, 2008).

To test the effects of hardening and granulation on the composition and leachability of wood ashes, the two selected ash samples, i.e. MA-9c and FA-2b (Section 2.2), were treated as follows. With regards to hardening,

subsamples of the ashes were hardened in the laboratory at ~22ºC for about 11 weeks, whereby a thin layer of ash was uniformly spread on top of plastic trays, turned over every other day and moistened with deionised water about three times a week. Every week, a small sample was taken from the trays and characterised for its acid neutralisation capacity (ANC – see Box 1). The "fully" hardened ashes were characterized for their elemental composition, content of total inorganic carbon and total organic carbon and the presence of crystalline mineral phases.

With regards to granulation, fresh ashes were firstly dried (100ºC), then milled and finally granulated (by means of a batch granulating machine). Granules were made from these ashes by adding deionised water or a solution of H_2SO_4. Additional granules were made from the hardened ashes, by adding deionised water. All samples were characterised for their elemental composition and the granules for their particle size distribution.

Box 1. Description of the acid neutralisation capacity applied in this project.

The acid neutralisation capacity (ANC): ANC measures the ability of a waste material to neutralise acidity under defined conditions (CEN/TS 14997:2006). The test consists of a stepwise titration with nitric acid (carried out at the L/S ratio 10 L/kg), during which the solution is continuously mixed and the pH of the solution is measured. The cumulative amount of acid added and the observed equilibrium pH can be plotted in a graph, i.e. the so-called "ANC curve". The test continues until the target pH is reached, for example pH 4 (ANC_4). Compliance with the standard method allows for direct comparison with other investigations. The shape of the curve is material-specific and it is sensitive to changes in the mineralogical structure in the material. As mineralogical changes during ash hardening are expected, the samples' ANC was monitored during the ash hardening process.

2.4 Ash leaching and geochemical modelling

Ash samples were characterised for their leaching behaviour through a series of leaching tests – Box 2 reports all the main characteristics and uses of these tests.

Batch leaching tests at the L/S ratio 2 L/kg were employed for all fresh ash samples except for two (i.e. FA-1 and FA-3), because of the insufficient size of the sample. Their results were compared with the relevant literature and the criteria for waste acceptance at landfills for "inert", "non-hazardous" and

"hazardous" waste (Directive 2003/33/EC). In addition to these tests, fresh MA-9c and FA-2b samples (i.e. fresh ashes) were also subjected to other leaching experiments, such as batch tests at L/S 10 L/kg, pH-dependent tests and column tests for the leaching of inorganic compounds. The results of these tests were used as inputs for geochemical modelling calculations. Samples MA-9c and FA-2b were characterized further for the leaching of PAHs and for the solubility of P in water and in neutral ammonium citrate.

Hardened and granulated MA-9c and FA-2b ashes were investigated by means of column tests for the leaching of inorganic compounds, and by batch tests assessing the solubility of P in water and neutral ammonium citrate. These results were used to investigate the effects of pre-treatments on the ash leaching behaviour.

Box 2. Description of the leaching tests applied in this project.

Batch tests (EN 12457-1,2: 2002): this test applies to granular waste materials and sludge. The material is crushed, placed in a bottle with deionised water (i.e. 2 L/kg and 10 L/kg) and then agitated for 24 hours. It is assumed that 24 hours ensure equilibrium or semi-equilibrium conditions in the system. The test is simple and fast, and it is often prescribed for compliance purposes, for example in the case of waste disposal (Directive 2003/33/EC, 2003). The leaching behaviour of different materials can be compared.

pH-dependent test (CEN/TS 14997:2006): this test applies to waste materials and is used to investigate the influence of pH on the leachability of inorganic constituents under equilibrium conditions. The material is crushed and mixed with deionised water at a defined L/S ratio (10 L/kg). Acid or a base is added to each of the mixtures (at least eight separate batches) up to a predefined pH value. The solution pH is controlled (manually or automatically) and adjusted to ensure that it remains stable throughout the experiment (48 hours). While the separate batches should at least cover the pH range 4-12, a slightly larger pH range was investigated during this PhD work (pH 2-13). Results from pH-dependent tests are often used as a basis for geochemical modelling, and so it has been done herein.

Column test (CEN/TS 14405: 2004): this test is applied to waste materials. The material is crushed, compacted in a column (ø: 5 cm; height: 30 cm) and then deionised water is pumped into it (up-flow saturated conditions; flow rate of 12 mL/h). Leachates are collected at specific cumulative L/S ratios,

typically in the range 0.1-10 L/kg. The test provides insights into the material's leachability as a function of the L/S ratio. The test is carried out under the hypothesis of equilibrium conditions. While the test typically lasts about a month, the operation of the columns in this study was prolonged to about five months in total, during which time leachates were collected regularly.

Additional columns were employed to test the presence of potential non-equilibrium conditions, which could in turn affect leaching from the ashes. These columns were packed and operated similarly to the "standard columns" but included two sets of flow-interruptions: one at L/S 2 L/kg and one at 50 L/kg. In each flow-interruption, the inlet flow was stopped and the system was left undisturbed for one week; next, the flow was restarted and one-quarter of the estimated pore volume was collected; afterwards, the inlet flow was stopped again and the procedure was repeated four times (i.e. one pore volume extracted). Similar flow-interruption set-ups have been used in other studies (e.g. Hyks et al., 2009b).

In order to investigate ash leaching behaviour at considerably higher L/S ratios (up to 2000 L/kg), additional columns, albeit shorter in the height (13 cm and 4.5 cm), were employed and operated similarly to the "standard columns".

Column test for leaching of PAHs (Nordtest TR576 (2004))**:** the test applies to waste materials and contaminated soils. The material is packed into a stainless steel column and equilibrated for six days under the continuous recirculation of a 0.005 M $CaCl_2$ and 0.5 g/L NaN_3 solution (L/S ~2 L/kg). At the end of the test, the leachates are extracted with acetone/pentane (1:1) and analysed for PAH concentrations, using a GC-MS (Reflab 4:2008, 2008). The test was used to investigate the solubility of PAHs from the ashes.

Phosphorus water solubility and extractable phosphorus in neutral ammonium citrate (Regulation (EC) 2003/2003, Methods 3.1.6 and 3.1.4 respectively): these tests apply to different fertiliser materials. Water-soluble P is determined after mixing the material with water in batch tests for 30 minutes at a temperature of 20-25ºC. Inversely, the fraction of P soluble in neutral ammonium citrate is determined after 60 minutes of mixing at a temperature of 65ºC. In both tests, leachates are filtered and analysed for the concentration of P. Water and neutral ammonium citrate are common solvents used to test phosphatic fertilisers, and they can be used for comparison purposes with other material types.

The mechanisms controlling leaching are diverse and material-specific. Geochemical model calculations can support the interpretation of the materials' leaching behaviour and indirectly predict the most likely minerals controlling the release of solubility-controlled elements. Box 3 provides a short explanation on the basic theory behind geochemical model calculations, and a list of a few relevant references is provided for further detail. While geochemical speciation has been often employed to model leaching from MSWI ashes (e.g. Astrup et al., 2006a; Hyks et al., 2009a; Meima and Comans, 1997; Polettini and Pomi, 2004), not many studies have focused on wood ashes (Allegrini et al., 2011; Komonweeraket et al., 2015; Steenari et al., 1998b, 1999a; van der Sloot and van Zomeren, 2010) and even fewer have comprehensively modelled major, minor and trace elements using a "multi-surface" modelling approach (Allegrini et al., 2011; van der Sloot and van Zomeren, 2010). In this PhD project, geochemical model calculations have been employed to support the description of the leaching mechanisms controlling the release from fresh MA-9c and FA-2b samples. The ORCHESTRA modelling framework (Meeussen, 2003) was employed, and thermodynamic data were retrieved from the MINTEQA2 database. The NICA-Donnan model (Kinniburgh et al., 1996) was used to model ion adsorption onto DOC, whereas the generalised two-layer model of Dzombak and Morel (1990) was used to calculate adsorption onto Fe-/Al-(hydr-)oxides. The selection of "plausible" mineral phases controlling the dissolution of major, minor and trace elements was carried out based on the calculated saturation indices, previous X-ray diffraction (XRD) analyses, common minerals observed in similar ash materials and results taken from other geochemical model predictions. More details about the definition of the geochemical model can be found in Paper **I** and **II**.

Box 3. Description of the geochemical model applied in this project.

Geochemical modelling: this is an indirect approach that aims at estimating the speciation of inorganic elements within a defined solution. During this PhD study, the so-called "multi-surface modelling approach" (Dijkstra et al., 2008) was employed to characterise leaching from wood ashes. The model incorporated mineral dissolution/precipitation, sorption onto Fe/Al (hydr-) oxides and DOC complexation. As the model represents a theoretical calculation, its accuracy depends on the quality and availability of all the data used as inputs as well as on the completeness and accuracy of the thermodynamic database. Mineral phases can be identified, but the actual

presence of these minerals in the dry materials should be verified by other means. The model, for example, can predict mineral phases formed during the water-particle interaction during leaching tests, which are not present in the original dry materials. Spectroscopic studies of the ashes may therefore be helpful in interpreting modelling results, and so it has been done herein through the use of X-ray diffraction and the analysis of data from other literature studies. Further information on geochemical modelling is available in Chandler et al. (1997), Dijkstra et al. (2008), Johnson et al. (1996), Meima and Comans (1997) and Van Zomeren and Comans (2004).

2.5 Leaching from soil columns at different ash dosages

To test the effects of wood ash application on percolating soil solutions, three different ash dosages were selected, i.e. 3, 9 and 30 tonne/ha, and spread on a single application. During these tests, fresh MA-9c ash was used. Current Danish legislation (DEPA, 2008) allows for a maximum wood ash dosage of 3 tonnes/ha/10y, which can be spread three times over a 75-year period (i.e. 9 tonnes/ha/75y). In this context, the ash dosages investigated herein were representative of three different application scenarios: a "typical case" (3 tonnes/ha), an "extreme case" (30 tonnes/ha) and an "intermediate case", where the 3x3 tonnes/ha (9 tonnes/ha) were spread on a single application.

The three wood ash dosages were applied on top of the O-horizon in one set of columns, and onto the A-horizon in another set of columns. This allowed testing the effects of wood ash applications on two slightly different soil horizons. Furthermore, in the herein investigated forest field, the depth of uppermost soil horizon (O-horizon) varies across the forest, suggesting that the case of wood ashes coming into direct contact with the below soil horizon is not impossible. Control columns (i.e. where no ash was applied) were also included. Moreover, as the application of wood ash has generally been reported to increase soil pH (which in turn can affect the mobility of the soil's constituents), two more columns (one for the O-horizon and one for the A-horizon), treated with 7 tonnes/ha of Ca-carbonate, were additionally included. The dosage of Ca-carbonate was chosen to have an ANC comparable to the highest wood ash dosage.

The O-horizon and A-horizon columns were packed in such a way as to reproduce depths (6 cm for O-horizon and 10 cm for A-horizon), bulk

densities (0.18 g/cm^3 for O-horizon and 0.65 g/cm3 for A-horizon) and moisture content (69 % for O-horizon and 32 % for A-horizon) similar to those observed in the field. To ensure a uniform distribution of deionised water pumped into the columns, a layer of acid-washed sand was employed below the soil, and up-flow percolating conditions were used. Water was pumped into the columns at a flow rate of ~50 mL/day for about three months, corresponding to ~2200 L/m^2 of water infiltrating into the soil. More details on the column set-up can be found in Paper **III**.

3 Characterisation of the ashes

In order to improve knowledge on locally produced fresh wood ashes, in relation to previous studies and local legislation, this section presents the composition of the 16 wood ash samples investigated during this PhD project. The effects of ash pre-treatments on the ash chemical properties are also presented. This section reports the main results from Paper **I** and **IV**.

3.1 Fresh ashes

Table 2 shows the composition of the 16 wood ash samples in comparison with selected literature studies, as reported in Paper **I**. The ash composition was relatively variable across the investigated samples, but overall it was comparable to typical ranges identified in other investigations for similar kinds of ashes (Etiégni et al., 1991; Etiégni and Campbell, 1991; Holmberg et al., 2000; Huang et al., 1992; Ingerslev et al., 2014; Narodoslawsky and Obernberger, 1996; Pöykiö et al., 2009, 2007; SLU, 2008; Steenari et al., 1999a; Supancic et al., 2014; Vassilev et al., 2014).

Fifteen wood ash samples out of the 16 investigated samples reported a composition that complied with content of contaminants as defined by current Danish legislation (DEPA, 2008): Cd: 20 mg/kg, Cr: 100 mg/kg, Ni: 60 mg/kg and Pb: 250 mg/kg. On the other hand, sample MA-5 ash largely exceeded the limits values for Cr (i.e. 217 mg/kg), indicating that this wood ash could not be applied on soil. In the samples where PAHs and Hg were analysed (MA-9c and FA-2b), the observed levels were below the limits set by Danish legislation (limits of 12 mg/kg for PAHs, and 0.8 mg/kg for Hg).

Electrical conductivity levels were mostly below 2800 mS/m (at L/S 5 L/kg): 1800 ± 1100 mS/m, with a median value of ~1400 mS/m (samples FA-2b, MA-9b and MA-9c are excluded from these averages). Current Danish legislation allows a maximum wood ash dosage of 3, 2 or 1 tonnes/ha/10y, if electrical conductivity is <2800 mS/m, between 2800 and 3200 mS/m or between 3200 and 3600 mS/m, respectively. Accordingly, most of the ashes investigated herein could be spread onto forest soil at a dosage of 3 tonnes/ha/10y.

Table 2. Composition of wood ash samples in comparison with typical literature values (primarily from grate-fired wood ashes), grouped by ash type. Minimum and maximum contents within each ash group are reported. Results are expressed in mg/kg dry weight, unless specified otherwise [BA: bottom ash; FA: fly ash; MA: mixed ash; n.m.: not measured; MC: moisture content; TOC: total organic carbon]. Paper **I**.

	BA – this study	BA - literature [a)]	FA – this study	FA - literature [a)]	MA – this study	MA - literature [a)]
samples	BA- 1, 2, 3		FA- 1, 2a, 2b, 3		MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	
MC [%]	8.07 - 29.5	19 - 31	28.1 - 60.2	0.2 - 52	0.0672 - 54.5	n.m.
TOC [%]	0.639 - 2.85	<0.05	7.39 - 32.8	1.6	0.472 - 19.1	0.52 - 13
NUTRIENTS AND MAJOR COMPONENTS						
Al	14300 - 16800	16000 - 40000	5920 - 11800	3600 - 26000	9020 - 16500	1700 - 40000
Ca	79400 - 162000	130000 - 300000	104000 - 263000	120000 - 280000	75600 - 214000	24000 - 340000
Cl	n.m.	<20 - 4700	n.m.	1600 - 11000	n.m.	210 - 14000
Cu	64.6 - 111	69 - 200	106 - 161	140 - 1100	71.4 - 195	78 - 440
Fe	4610 - 6570	6000 - 26000	2880 - 8300	1500 - 59000	5000 - 15000	1600 - 25000
K	35800 - 73200	40000 - 47000	40000 - 60300	50000 - 160000	35800 - 80000	25000 - 250000
Mg	16500 - 20600	12000 - 44000	19300 - 32900	20000 - 50000	12800 - 39900	16000 - 80000
Mn	3470 - 19400	4300 - 27000	4030 - 30300	1300 - 23000	3060 - 19000	3500 - 19000
N	<400	150	1670 - 4930	2500 - 2500	<400 - 2600	600 - 5000
Na	8260 - 11100	4800 - 12000	6650 - 12000	3100 - 8300	6590 - 11300	500 - 37000
P	8310 - 17400	7200 - 22000	10200 - 22900	4300 - 20000	10000 - 26500	3200 - 21000
S	153 - 967	270 - 2400	4210 - 15300	5800 - 25000	1540 - 5950	1300 - 52000
Si	208000 - 273000	120000 - 250000	45600 - 124000	11000 - 82000	124000 - 271000	17000 - 260000
Zn	73.9 - 234	65 - 950	446 - 1120	370 - 40000	18.4 - 737	26 - 2800
TYPICAL ELEMENTS OF ENVIRONMENTAL CONCERN						
As	2.17 - 3.19	1.4	2.68 - 6.98	1.5 - 24	2.24 - 7.67	0.09 - 74
Ba	802 - 1400	1600 - 2200	797 - 2320	1200 - 4300	684 - 1880	420 - 2700
Cd	0.158 - 0.467	<0.2 - 5.7	7.32 - 16.3	5.1 - 34	0.109 - 8.82	<2 - 31
Co	4.23 - 7.3	6.7 - 11	5.79 - 9.69	11 - 13	3.76 - 7.72	<3 - 77
Cr	24.9 - 69.5	64 - 320	26.5 - 62.7	32 - 290	22 - 217	14 - 260
Hg	n.m.	0.02 - 0.1	n.m.	1.7	n.m.	0.06 - 1.2
Mo	1.06 - 1.84	1 - 5.8	1.46 - 4.29	8.6 - 16	1.14 - 4.36	1.2 - 120
Ni	27.4 - 38.6	22 - 200	22.4 - 52.5	19 - 74	31.2 - 44.7	12 - 500
Pb	4.74 - 79.8	4 - 40	10.7 - 73.8	25 - 470	0.682 - 36.4	13 - 130
Sb	0.496 - 3.48	0.86 - 2.3	0.721 - 5.83	1.7 - 3	0.69 - 3.11	0.71 - 94
Se	<16.7	<0,1	<16.7	0.24 - 2.1	<16.7	16
Sn	<0.305 - 1	11 - 16	1.21 - 6.37	15 - 22	1.07 - 3.14	2.1 - 4.4
Sr	466 - 783	610 - 710	578 - 1240	750 - 2100	449 - 959	320 - 1200
Tl	0.172 - 0.473	n.m.	0.975 - 1.98	n.m.	0.0624 - 1.49	n.m.
V	10.4 - 18.4	26 - 64	6.75 - 18.2	5.1 - 43	11.3 - 18.6	3.4 - 56

a): Etiégni et al., 1991; Etiégni and Campbell, 1991; Holmberg et al., 2000; Huang et al., 1992; Ingerslev et al., 2014; Narodoslawsky and Obernberger, 1996; Pöykiö et al., 2009, 2007; SLU, 2008; Steenari et al., 1999; Supancic et al., 2014; Vassilev et al., 2014.

The ANC_4 of MA-9c and FA-2b was observed at 4.7 and 13 $meqH^+/g$, respectively (Paper **I**), in line with the levels reported by Freire et al. (2015) for similar types of ashes. In comparison, the ANC_4 of laboratory-grade Ca-carbonate was observed at ~19 $meqH^+/g$ (Paper **III**), i.e. somewhat larger than the ANC_4 of the ashes. In general, large variations in the neutralisation value have been reported across different wood ash samples, for instance

between 13.2 and 92.4 % of pure calcium carbonate in Vance (1996) and Demeyer et al. (2001). These results suggest that different ashes applied at similar soil application dosages are likely to result in considerably different liming effects.

XRD analyses in Paper **I** indicated the presence of crystalline calcite, lime, portlandite, quartz, ankerite and magnesite in the case of MA-9c, whereas calcite, portlandite, quartz, periclase, maghemite and calcium silicate were proposed for FA-2b. These results were in overall agreement with the minerals reported by Holmberg and Claesson (2001).

3.2 Pre-treated ashes

Paper **IV** indicated that the elemental composition of the ashes is not affected by the granulation process, unless additives are included in the water infusion (e.g. H_2SO_4), and that relatively hard granules can be generated (i.e. barely breakable by finger-pinching). These results overall suggest that (i) specific additives may be added during granulation to adjust the nutrient value of the ashes to specific soil needs and (ii) ash handling and spreading would likely be more practical (e.g. by means of a mechanical spreader) and with less dust formation, if carried out with granules rather than loose materials.

During hardening, the thermodynamically unstable wood ashes undergo a series of chemical reactions when exposed to atmospheric moisture and carbon dioxide. As indicated by Steenari and Lindqvist (1997), depending on the availability of the reactants, several major reactions can occur during hardening, namely the formation of hydroxides, carbonates, gypsum, ettringite, hydrated silicates and aluminium silicate phases. As a result of the relatively high contents of Ca reported in wood ashes, typically in the range of 2.4-34 % (Table 2), the aforementioned reactions are likely to involve Ca-bearing minerals. The elemental composition of hardened ashes was comparable to fresh ashes, except for the higher content of inorganic carbon. The latter increased from 0.81 % (fresh ashes) to 2.1 % in MA-9c ashes, whereas in the case of FA-2b ashes it increased from 0.89 % (fresh ash) to 4.82 %. Furthermore, while the XRD results from fresh ashes indicated the presence of crystalline lime (CaO) and portlandite ($Ca(OH)_2$), these minerals were not identified in hardened ashes (Paper **IV**). These results indicated that lime and portlandite were transformed into calcite, in accordance with the processes described by Steenari and Lindqvist (1997).

Paper **IV** investigated developments in the ash ANC curve during the circa eleven weeks of lab-hardening – see Figure 1. While the shape of the ANC curve changed rapidly within the first one to two weeks of hardening, relatively small differences in the $ANC_{4.5}$ of the ashes were observed between fresh and hardened ashes. The $ANC_{4.5}$ of fresh ashes was slightly reduced after hardening, from 5.3 to 4.5 $meqH^+/g$ for MA-9c and from 13 to 11 $meqH^+/g$ for FA-9c. The overall liming capacity of the ashes is therefore maintained after hardening.

Worth noticing that Figure 1 additionally shows that a slight decrease in the equilibrium pH of hardened ashes was also observed - see how the first point of ANC curve slowly decreases during hardening. Hardening is a spontaneous process governed by the thermodynamic instability of the ashes, and it will occur anyway, under controlled conditions or in the field. It is a relatively fast and simple process that takes place as soon as favourable conditions occur (i.e. availability of carbon dioxide, moisture and ash reactants), and it seems reasonable that it should be carried out under controlled conditions regardless of the end use of the ashes, i.e. whether it is applied onto soil or landfilled. Some delays during field scale hardening should however be expected compared with lab-hardening, due to the less optimal exposure to moisture and carbon dioxide. More details on the effects of hardening on the ash leaching are presented in Section 4.4.

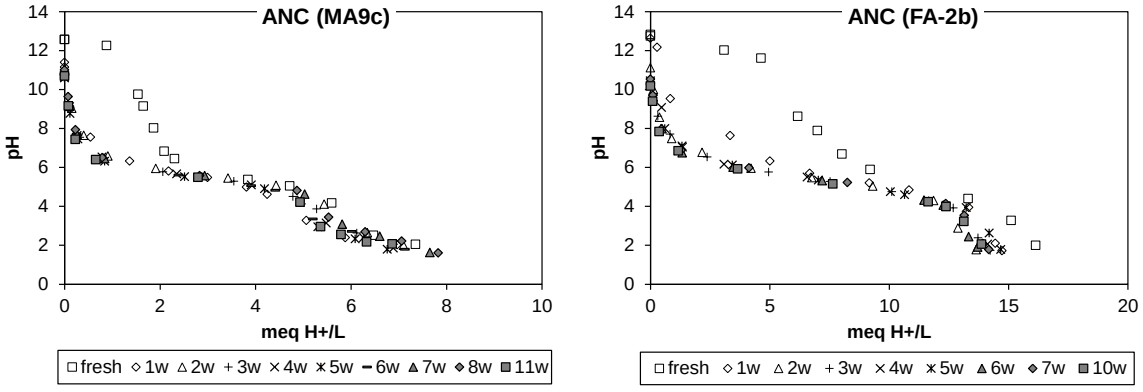

Figure 1. Development of the ANC curve during lab-hardening of MA-9c and FA-2b ashes. [fresh: fresh ashes; 1÷11w: weeks of hardening]. Adapted from Paper **IV**.

4 Leaching from wood ash

To provide a comprehensive evaluation of ash leaching behaviour, wood ashes were characterised by means of a series of standard leaching methods (see Box 3), the results of which were then used as inputs for geochemical model calculations. The source-term release from the ashes was estimated for different pH conditions and on the basis of short-/long-term leaching. The influence of hardening and granulation on the ash chemistry, on the nutrient and contaminant leaching and on the liming potential was investigated. The results were compared with relevant literature and Danish legislation. In the following sub-sections, leaching data and geochemical modelling from untreated ashes (fresh ashes) refer to Paper **I** and **II**, while leaching from granulated and hardened ashes refers to Paper **IV**.

4.1 Fresh ashes: batch leaching

The batch leaching of Danish ashes (14 samples) was overall comparable to typical literature ranges for similar types of ashes (Freire et al., 2015; Pöykiö et al., 2009; Steenari and Karlfeldt Fedje, 2010; Supancic et al., 2014; van der Sloot and van Zomeren, 2010) – see Table 3. If the same leaching data would be compared with landfill acceptance criteria (Directive 2003/33/EC, 2003), only one sample would be classified as "inert", seven samples as "non-hazardous" and six samples as "hazardous" (mainly because of the concentration levels of Cr and Se – see footnote for Table 3). In particular, the ash samples selected for a more detailed characterisation, i.e. MA-9c and FA-2b, would be classified as "non-hazardous waste". This is a noteworthy finding, as the same ashes could be applied otherwise onto forest soil.

Leaching of PAHs was observed below LOQ levels (at L/S 2.6 L/kg) for both MA-9c and FA-2b ashes (Paper **I**). Likewise, low leaching of PAHs was reported from Swedish wood ash pellets by Enell et al. (2008) during column experiments, despite their different operating conditions (leachant media, i.e. deionized water during the first part of the experiment and acidified water afterwards, and L/S ratio, i.e. up to ~1650 L/kg).

Table 3. Compliance leaching test results in comparison with literature values, grouped by ash type. Results are expressed in mg/kg dry weight, unless specified otherwise. Minimum and maximum contents within each ash group are reported. [BA: bottom ash; FA: fly ash; MA: mixed ash; n.m.: not-measured; *: indicates that the value only refers to FA-2b or MA-9c]. Selected limit values are added in the footnote [b)] as reference. Adapted from Paper **I**.

	BA (L/S 2)	FA (L/S 2)	FA (L/S 10)	MA (L/S 2)	MA (L/S 10)	BA- Literature [a)] (L/S 10)	FA- Literature [a)] (L/S 10)
samples	BA- 1, 2, 3	FA- 2a, 2b	FA-2b	MA- 4, 5, 6, 7, 8, 9a, 9b, 9c, 10	MA-9c	-	-
pH [-]	12.9 - 13.3	13.1 - 13.9	12.7	11.9 - 13.8	12.7	10.7 - 13.5	11.9 - 13
EC [mS/cm]	12 - 43	64 - 69	19.9	9.2 - 67	14.3	1.466 - 15.88	3.7
DOC	68 - 120	78 - 160	86	6.6 - 630	12	-	0.192 - 29
NUTRIENTS AND MAJOR COMPONENTS							
Al	0.72 - 8.6	<0.25	<1.2	<0.25 - 24	<1.2	<1 - 35	5.3
Ca	22 - 220	16 - 320	4700	<8 - 1500	7000	100 - 8980	2700 - 10790
Cl	77 - 320	2500 - 3400	3200	84 - 3600	750	1.21 - 800	7000 - 34000
Cu	0.013 - 0.23	0.025 - 0.15	0.066	<0.0043 - 0.55	<0.021	0.03 - <0.5	0.08 - <0.5
Fe	<0.012	<0.013	<0.062	<0.017	<0.062	0.03 - <0.5	0.034 - <0.5
K	2700 - 14000	25000 - 29000	28000	4400 - 39000	9500	384 - 14200	3413 - 30000
Mg	<0.032	<0.034	0.26	<0.032 - 1.5	0.43	<0.2 - 3	<0.2 - 2.35
Mn	0.011 - 0.065	<0.011 - 0.018	<0.053	<0.011 - 0.46	<0.053	0.02 - 0.14	0.009 - <0.2
Na	280 - 1000	2200 - 3500	2400	340 - 4100	1000	42 - 204	700 - 6000
P	<0.59 - 1.2	<0.61	<2.9	<0.59 - 1.6	<2.9	<5	0.13
S	-	1700*	1600*	420*	410*	7 - 1040	500 - 16700
Si	<0.35 - 230	<0.36 - 3.3	<1.8	<0.35 - 570	<1.8	<10 - 122	5.6 - 38
Zn	<0.063	0.24 - 0.38	0.31	<0.067 - 1.9	2.8	<0.2	<0.2 - 51
TYPICAL ELEMENTS OF ENVIRONMENTAL CONCERN							
As	<0.0044 - 0.048	<0.0046 - 0.005	<0.022	<0.0044 - 0.61	<0.022	<5	0.044
Ba	0.059 - 1.4	0.22 - 0.59	2.9	0.015 - 0.75	5.9	1.27 - 131	2.7 - 145
Cd	<0.0014	<0.0014	<0.007	<0.0015	<0.0069	<0.03	0.0004 - <0.02
Co	<0.001 - 0.0024	<0.001 - 0.0032	<0.005	<0.001 - 0.023	<0.005	<0.2	0.001 - 0.001
Cr	0.13 - 5.7	1.2 - 6.2	6.2	<0.0046 - 4.5	0.29	0.08 - 0.91	0.01 - 38
Hg	n.m.	n.m.	n.m.	n.m.	n.m.	-	-
Mo	0.25 - 0.38	0.46 - 1.1	1.1	0.25 - 1.7	0.26	<0.2	0.78 - 5.4
Ni	0.03 - 0.067	<0.0046 - 0.28	1.1	0.023 - 0.87	0.94	<0.5	0.009 - <0.5
Pb	<0.0013 - 0.014	0.011 - 0.054	0.09	<0.0014 - 0.021	0.036	0.11 - <0.5	<0.5 - 157
Sb	<0.0024 - 0.0035	<0.0025	<0.012	<0.0024 - 0.11	<0.012	-	<0.05 - 0.18
Se	<0.014 - 0.027	0.23 - 0.68	0.34	0.053 - 0.54	0.2	-	0.14 - 1.5
Sn	<0.0025	<0.0026	<0.012	<0.0025 - 0.006	<0.012	-	0.004 - 0.004
Sr	0.1 - 3.8	3.3 - 11	56	0.073 - 26	61	-	33
Tl	<0.00036 - 0.00078	<0.00037	<0.0018	<0.00036 - 0.0008	<0.0018	-	-
V	0.0019 - 0.51	0.0019 - 0.0019	<0.0073	<0.0015 - 3.2	<0.0073	<0.1	0.035

[a)] included literature: Freire et al. (2015); Pöykiö et al. (2009); Steenari and Karlfeldt Fedje (2010); Supancic et al. (2014); Van Der Sloot and Van Zomeren (2010).

[b)] Directive 2003/33/EC: leaching criteria (L/S 2 L/kg) for the acceptance of waste at landfills
for inert waste (mg/kg dry weight): As: 0.1; Ba: 7; Cd: 0.03; Cr tot: 0.2; Cu: 0.9; Mo: 0.3; Ni: 0.2; Pb: 0.2; Sb: 0.02; Se: 0.06; Zn: 2; chloride: 550; sulphate: 560; DOC: 240.
for non-hazardous waste (mg/kg dry weight): As: 0.4; Ba: 30; Cd: 0.6; Cr tot: 4; Cu: 25; Mo: 5; Ni: 5; Pb: 5; Sb: 0.2; Se: 0.3; Zn: 25; chloride: 10000; sulphate: 10000; DOC: 380.

In accordance with the generally low releases of P observed in the literature for wood ashes, all the herein investigated samples demonstrated low releases of P – see Table 3. Inversely, considerably higher released amounts were

found in the case of neutral ammonium citrate extractions (Paper **IV**), where differences of about three orders of magnitude were observed compared to the water solubility levels, i.e. 4.8 g/kg for MA-9c (i.e. ~48% of the total P content) and 7.0 g/kg for FA-2b (i.e. ~33% of the total P content), an effect that may be connected to the dissolution of apatite minerals. While apatite minerals have been reported to dissolve during neutral ammonium citrate extractions (e.g. Brod et al., 2015b; Yusiharni et al., 2007), the potential presence of these minerals in the herein investigated ashes was proposed by the geochemical modelling calculations in Paper **I** (see Section 4.2). In support of these calculations, apatite minerals have been reported in other wood ash studies after XRD scanning (e.g. Brod et al., 2015a; Steenari and Lindqvist, 1997; Vassilev et al., 2013). Relatively similar releases of P have been presented by other wood ash investigations using neutral ammonium citrate as an extracting solvent, i.e. in the range of 57-78 % of the total P content (Brod et al., 2015b; Erich, 1991; Yusiharni et al., 2007). As the solubility of P in neutral ammonium citrate is one of the criteria used to assess its bioavailability (Kruger and Adam, 2015), these results suggest that wood ashes appeared as a potentially valuable source of P if applied onto soil.

4.2 Fresh ashes: pH-dependent leaching

Wood ash leaching was affected significantly by pH conditions – see Figure 2 for a selected list of elements (data from Paper **I**). The two investigated ashes (MA-9c and FA-2b) presented generally similar development in the chemical composition of the leachates across the investigated pH range, as well as relatively similar concentration levels. In particular, acidic conditions in the pH 3-5 range (relevant for acidic Danish forest soils conditions – see Balstrøm et al. (2013)) increased the released amounts of Cd, Mg, Zn and P of at least two orders of magnitude relative to natural ash pH conditions (e.g. in the case of MA-9c the levels increased from <0.01 to ~1.0 mg/kg for Cd, from 0.6 to ~5000 mg/kg for Mg, from 2 to ~100 mg/kg for Zn, and from 4 to ~1000 mg/kg for P). At the same time, the release of Mo and Cr decreased (e.g. in the case of MA-9c the levels decreased from 0.2 to 0.02-0.1 mg/kg for Mo and from 0.3 to 0.01-0.1 mg/kg for Cr). The leaching of Cl, K, Na and S was relatively pH-independent (e.g. in the case of MA-9c, ~0.8 g/kg for Cl, ~10-20 g/kg for K, ~0.8-2 mg/kg for S and ~0.8-3 mg/kg for Na). More

detailed information about trends and concentration levels can be found in Paper **I**.

Based on the results of pH-dependent tests, and under the assumption that ash leaching would be governed by the soil's pH conditions, Paper **I** estimated the expected release of nutrients and contaminants from MA-9c and FA-2b ashes in the case of a hypothetical application onto acidic soil at a dosage of 3 tonnes/ha. In this assessment, the source-term release of Cd was considered to be potentially problematic with regards to the quality of the topmost centimetre of soil, whereas the expected release of As, Ba, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sn, Tl and Zn was low – see more details in Paper **I**. This kind of evaluation can offer a preliminary assessment of ash source-term release in different pH conditions, which may then be used for further soil investigations addressing the interaction between these compounds and the specific soil.

Geochemical modelling calculations (see model predictions in Figure 2) indicated the minerals most likely to be in equilibrium with the ash leachates: ankerite, $Ba_{0.5}Sr_{0.5}SO_4$, birnessite, brucite, calcite, calcium silicate, calcium silicate hydrates, Cl-pyromorphite, $Cu(OH)_{2(s)}$, gibbsite, hydroxyapatite, leucite, magadiite, lime, maghemite, magnesite, microcline, octacalcium phosphate, $PbMoO_4$, portlandite, quartz, willemite, zincite and $ZnO_{(s)}$. These minerals were in general agreement with other wood ash investigations (Holmberg and Claesson, 2001) and geochemical modelling studies carried out on wood ashes (Paper **I**; Allegrini et al., 2011; Steenari et al., 1998b, 1999; van der Sloot and van Zomeren, 2010) and MSWI ashes (Astrup et al., 2006b; Dijkstra et al., 2006a; Hyks et al., 2007).

Mineral dissolution could describe adequately the leaching of major elements such as Ba, Ca, Mg, Si, P (as PO_4^{3-}) and S (as SO_4^{2-}). Readily soluble phases were likely to govern the release of K, Cl and Na, as indicated by the relatively pH-independent trends and the good correlation with the results from batch tests at L/S 2 and 10 L/kg. With regards to trace elements, the use of the so-called "multi-surface" modelling approach (Dijkstra et al., 2008) allowed an acceptable description of elements such as Cr, Cu, Ni and Zn. Since DOC levels in the herein investigated wood ash leachates were considerably lower than in MSWI ash leachates (about 0.28-3.4 mg/L in Paper **I**, against the 10-100 mg/L observed in Dijkstra et al. (2006b), Hyks et al. (2007), Meima and Comans (1997) and Van Zomeren and Comans (2004)), the relative importance of DOC complexation processes in the

description of wood ash leaching was also lower, albeit not negligible. Adsorption to Al/Fe (hydr-)oxides improved the model's predictions for the levels of trace elements in the solution.

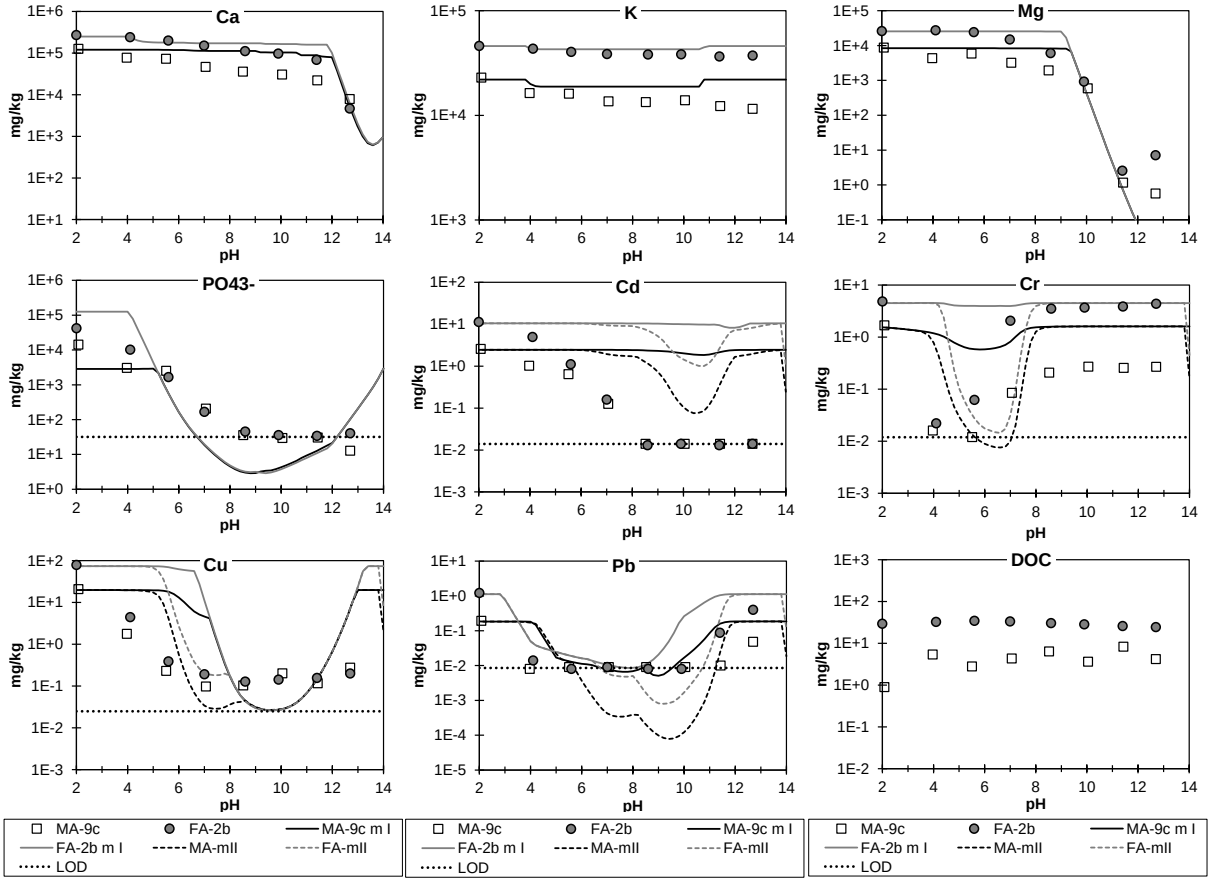

Figure 2. pH-dependent leaching test results from MA-9c and FA-2b ashes in comparison with the geochemical model predictions for selected major, minor and trace elements. More elements can be found in Paper I. [m I and m II: model I and model II as defined in Paper I]. Adapted from Paper **I**.

4.3 Fresh ashes: long-term leaching

In the case of wood ash applications, depending on site-specific conditions, relatively large amounts of water may infiltrate through forest soil. The Danish forest soil sample collected during this PhD study, for example, would experience a net rainfall infiltration of about 270 L/m^2/y (Hansen et al., 2017). Assuming the case of wood ashes spread at 3 tonnes/ha, the annual amount of infiltrating water passing through the ash would result in a theoretical L/S ratio of ~900 L/kg/y. While this is a very approximate calculation, it nevertheless highlights that standard column tests at cumulative L/S 10 L/kg may not be sufficient to investigate ash leaching

behaviour at the considerably higher L/S ratios that the ash may experience in the field. While the operating conditions of column tests may not directly represent the conditions which the ash will experience when applied onto soils, column data can provide insights into ash solubility and leaching mechanisms and may be used to estimate source-term releases.

Column tests were employed in Paper **II** to investigate ash leaching under the conditions defined by the CEN/TS 14405:2004 method and under a slightly modified version of it, which allowed to test considerably higher L/S ratios, i.e. up to L/S 2000 L/kg. Despite the different operating conditions of the individual columns, at every chosen L/S ratio the composition of the leachates was comparable across the different columns, thus enabling the description of ash leaching as a function of the L/S ratio irrespective of the specific column. Similarly, geochemical model predictions could be described as a function of the L/S ratio, too.

The list of mineral phases predicted during geochemical model calculations for MA-9c leachates was comparable to the list of minerals predicted for FA-2b leachates and was in overall agreement with the minerals proposed in the literature for similar kinds of ashes (Paper **I**; Allegrini et al., 2011; Freire et al., 2015; Magdziarz et al., 2016; van der Sloot and van Zomeren, 2010; Vassilev et al., 2013). More specifically, barite, calcite, clinoenstatite, forsterite, hilgenstokite, jennite, merwinite, portlandite and wollastonite were suggested to be in equilibrium with both MA-9c and FA-2b leachates. In addition to these mutual minerals, CO_3-hydrotalcite and diaspore were indicated for MA-9c, while akerminite, brucite, goethite and tobermorite were predicted for FA-2b.

The dissolution of the predicted minerals approximated well the analytical concentration of Ca, Mg, Al, Ba, S, Si and Fe, indicating that a relatively limited selection of minerals was sufficient to describe leaching behaviours for the different L/S ratios (see Table 4), and that mineral solubility plays an important role in the release of Ca, Mg, Al, Ba, S, Si and Fe. The release of Cl, K and Na reflected the leaching behaviour of readily soluble compounds, in that their concentration rapidly decreased with the L/S ratio, i.e. decreases in the range of two to three orders of magnitude by the L/S 1.0-10 L/kg. Similar drops in concentrations were observed for S, albeit a little more pronounced in the case of MA-9c ashes. DOC complexation had a minor, often negligible, contribution to the description of concentration levels of trace elements, such as Pb and Ni; the largest effect, albeit still relatively

small, was observed for Cu in the FA-2b leachates before the L/S ratio 2 L/kg, where about 6-14 % of the Cu in the solution was calculated to be complexed with DOC. Despite these are relatively low numbers compared to, for example, the >95 % observed by Olsson et al. (2007) in the case of MSWI bottom ashes, it should however be noted that the herein included DOC complexation model was used in its default setup, as no sample-specific parameters were available.

The calculated leached "standard alkalinity" (defined as 2 $[CO_3^{-2}]$ + $[HCO_3^-]$ + $[OH^-]$, where the square brackets represent the molar concentration of the different species) showed that relatively large amounts of alkaline species were released during long-term leaching (L/S 1000 L/kg), corresponding to about 85 % (MA-9c) and 64 % (FA-2b) of the ANC_4 of MA-9c and FA-2b, respectively. Accordingly, an overall decrease in pH of about three units was observed between the beginning (pH ~13.5) and the end of the column experiment (pH 10.5-11.0).

The influence of flow-interruptions on ash leaching was more evident for the MA-9c columns, suggesting the presence of non-equilibrium conditions during their operation. The influence on FA-2b leaching was generally very modest, indicating that these columns were operated close to equilibrium conditions. During flow interruptions, the pH of MA-9c leachates increased by about 0.6-0.7 pH units. At the same time, a considerable increase in the concentration levels of K, Na and Al was also observed: during the first flow-interruption (L/S 2 L/kg), concentrations of K, Na and Al increased by about six, six and 37 times, respectively, whereas during the second flow-interruption they increased by about seven, nine and three times, respectively. While geochemical model calculations suggested no specific mineral with the potential to describe these increasing concentrations, it was suspected that K, Na and Al may have dissolved from (hydr-)oxides, carbonates and silicates species (Johnson et al., 1995), the dissolution of which could in turn have promoted the observed pH increase. The concentrations of Ca and Ba also increased during flow-interruptions, but their mineral equilibrium was maintained compared to continuous columns. The effect of flow interruptions on other elements was small and unlikely to be caused by changes in mineral solubility.

Table 4. Most relevant minerals for leaching control of Ca, Mg, Al, Ba, SO_4^{2-}, Si and Fe in MA-9c and FA-2b leachates at selected L/S ratio ranges [+++: very accurate description of the observed concentrations; ++: good description of the observed concentrations; +: limited/scarce description of the observed concentrations; ---: no mineral with the potential to describe the observed concentrations]. Adapted from Paper **II**.

			MA-9c						
			L/S ratio (L/kg)						
	Mineral name	**Chemical formula**	**0-10**	**10-20**	**20-50**	**50-100**	**100-250**	**250-500**	**500-1000**
Ca	jennite	$Ca_9Si_6O_{18}(OH)_6{\cdot}8H_2O$	+++	+++	+++	+++	+++	+++	+++
	hilgenstokite	$Ca_4P_2O_9$	+++	+++	+++				
	portlandite	$Ca(OH)_2$	+++	+++	+				
	merwinite	$Ca_3Mg(SiO_4)_2$	+++	+++	+++				
	calcite	$CaCO_3$		+++	+++	+++	+++	+++	+++
Mg	CO_3-hydrotalcite	$Mg_6Al_2CO_3(OH)_{16}{\cdot}4(H_2O)$	+++	+++	+++	+++	+++	+++	+++
	clinoenstatite	$Mg_2Si_2O_6$				++	+++	+++	+++
	forsterite	Mg_2SiO_4;				+++	+++	+++	+++
Al	CO_3-hydrotalcite	$Mg_6Al_2CO_3(OH)_{16}{\cdot}4(H_2O)$	+++	+++	+++	+++	++		
	diaspore	α-AlO(OH)					++	+++	+++
Ba	barite	$BaSO_4$	+++						
SO_4^{2-}	barite	$BaSO_4$	+++						
Si	jennite	$Ca_9Si_6O_{18}(OH)_6{\cdot}8H_2O$	+++	+++	+++	+++	+++	+++	++
	merwinite	$Ca_3Mg(SiO_4)_2$	+++	+++	+++				
	clinoenstatite	$Mg_2Si_2O_6$				+++	+++	+++	+++
	wollastonite	$Ca(Mg,Fe)SiO_4$							++
Fe	---	---							

			FA-2b							
			L/S ratio (L/kg)							
	Mineral name	**Chemical formula**	**0-10**	**10-20**	**20-50**	**50-100**	**100-250**	**250-500**	**500-1000**	**1000-2000**
Ca	jennite	$Ca_9Si_6O_{18}(OH)_6{\cdot}8H_2O$	+++	+++	+++	+++	+++	+++	+++	++
	tobermorite	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$		+++	+++	+++	+++	+++	+++	++
	calcite	$CaCO_3$	+	+	+	++	+++	+++	+++	+++
	portlandite	$Ca(OH)_2$	+++	+	+	+				
	hilgenstokite	$Ca_4P_2O_9$	+++	+++	+	+++				
	merwinite	$Ca_3Mg(SiO4)_2$	+++	+++	+	+				
Mg	forsterite	Mg_2SiO_4;			++	+++	+++	+++	+++	+++
	akerminite	$Ca_2MgSi_2O_7$	+	+	+	+++	+++	+++	+++	+++
	clinoenstatite	$Mg_2Si_2O_6$					+	+++	+++	+++
	brucite	$Mg(OH)_2$	++	+		+	++	++	++	++
Al	---	---								
Ba	barite	$BaSO_4$	+++	+++	+++	+++				
SO_4^{2-}	barite	$BaSO_4$	+++	+++	+++	+++				
Si	merwinite	$Ca_3Mg(SiO_4)_2$	+++							
	tobermorite	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$	+++	+++	+++	+++	+++	+++	+++	++
	akerminite	$Ca_2MgSi_2O_7$		+	+++	+++	+			
	wollastonite	$Ca(Mg,Fe)SiO_4$							+	+++
	jennite	$Ca_9Si_6O_{18}(OH)_6{\cdot}8H_2O$							++	+
	clinoenstatite	$Mg_2Si_2O_6$			+	++	+++	+++	+++	+++
	forsterite	Mg_2SiO_4;			+	++	+++	+++	+++	+++
Fe	goethite	α-FeO(OH)	+	+	+	+	+			

Table 5 reports the calculated column released amounts of selected nutrients and potential contaminants for the cumulative L/S 1000 L/kg and L/S 10 L/kg, as reported in Paper **II**. The table indicates that the estimation of wood ash releases at relatively high L/S ratios may be largely underestimated if based on leaching tests carried out at relatively low L/S ratios, especially in the case of Al, Ba, Ca, Cr, Mg, Sb, V and Zn, where differences of at least one order of magnitude were observed between the cumulative releases at L/S 10 and 1000 L/kg. Furthermore, it was demonstrated that simple batch tests (single step or sequential) may not be sufficient to capture developments in leaching behaviour as a function of the L/S ratio (for example in the case of Cr, Sb, V and Sr) – see Paper **II**.

Table 5. Calculated cumulative releases from column tests, grouped into nutrients and elements of typical environmental concern. The values are expressed as fractions (%) of the total contents removed from the ashes. Adapted from Paper **II**.

PLANT NUTRIENTS						ELEMENTS OF TYPICAL ENVIRONMENTAL CONCERN					
	Released mass	MA-9c 10 L/kg	MA-9c 1000 L/kg	FA-2b 10 L/kg	FA-2b 1000 L/kg		Released mass	MA-9c 10 L/kg	MA-9c 1000 L/kg	FA-2b 10 L/kg	FA-2b 1000 L/kg
Al	%	0.0031	1.6	0.0032	0.64	**As**	%	0.24	<14	<0.11	<9.8
Ca	%	6.5	40	2.6	43	**Ba**	%	4.5	18	0.21	18
Fe	%	<0.0003	<0.019	0.0006	<0.030	**Cd**	%	<0.049	<4.9	<0.012	<1.2
K	%	39	64	89	88	**Cr**	%	<0.025	4.1	11	18
Mg	%	0.0010	1.1	0.0004	0.30	**Cu**	%	<0.011	<12	0.18	<6.2
Mn	%	<0.0001	<0.0099	<0.0001	<0.0067	**Mo**	%	≈16	<100**	34	<100**
N-NO_3^-	%	0.43	<2.6	3.5	8.9	**Ni**	%	<0.27	<27	≈0.23	<26
Na	%	16	40	41	53	**Pb**	%	0.24	≈0.41	0.17	0.81
P	%	<0.0020	<0.20	≈0.0015	<0.095	**Sb**	%	<0.064	19	<0.033	16
S	%	64	100**	79	100**	**V**	%	<0.040	29	≈0.079	21
						Zn	%	0.41	1.4	0.050	1.1

4.4 Pre-treated ash leaching

Figure 3 and 4 show developments in the concentration of selected elements (i.e. Ca, K, P, S, As, Cd, Pb, Sb, Zn and pH) during the leaching of granulated and hardened ashes.

FA-2b granules made from the fresh ashes were qualitatively hard (barely breakable by finger-pinching) and small (70-75 % dry weight between 1 and 2 mm) and their column leaching presented relatively modest variations compared to untreated FA-2b ashes. MA-9c granules were also hard, albeit larger than the FA-2b granules. The specific surface area of the granules appeared to be an important parameter in view of leaching. More specifically, while column leachates from MA-9c granules reported levels of Ba, Ca, Fe, K, Na and Zn up to one order of magnitude lower than untreated MA-9c ashes, FA-2b granules reported more modest effects (generally limited to a

twofold factor). An increased leaching of S was observed from the MA-9c granules spiked with H_2SO_4, thereby suggesting that other additives may be also added to adapt the ashes to specific nutrient (or strength) needs. No evidence of higher leaching of S was however observed in the case of FA-2b ashes spiked H_2SO_4 compared to the other FA-2b samples, probably because of the relatively low amounts of S being added (see Paper IV for a detailed description of the granulation process with addition of H_2SO_4).

During hardening, lime is hydrated into portlandite, which will then react with atmospheric carbon dioxide to form calcite – see Section 2.3 for more details. Since the solubility of calcite is about a hundred times lower than lime and portlandite (Steenari and Lindqvist, 1997), a reduction in the ash release of alkalinity can be observed. Accordingly, Paper **IV** reported both a decrease in leached alkalinity compared to granules made from fresh ashes and a considerable decrease in concentration levels of Ca (i.e. <6 mg/L in the leachates from hardened ashes against the ~1000 mg/L in the leachates from untreated fresh ashes). Besides Ca, hardening also affected the release of other elements: the leaching of Ba, Pb and Zn was reduced (below or close to limit of quantitation levels), whereas the leaching of As, P, Sb, Si, V and Mg was enhanced. The initial leaching of K and Na was reduced in the case of hardened MA-9c ashes, while the effect on hardened FA-2b ashes was very modest. Paper **IV** combines these observations with the results from other wood ash and MSWI ash studies in order to identify the key leaching mechanisms controlling the release of these elements. Granulation of hardened ashes had a very limited effect on leaching compared to the un-granulated hardened ashes.

The amounts of P released after neutral ammonium citrate extractions were practically unaffected by granulation and hardening (Paper **IV**), which in turn suggests that the ash solubility of P in soil application would be the same, irrespective of whether wood ashes are fresh or hardened. In general (including the results of both pre-treated and untreated samples), MA-9c and FA-2b ashes released about 5.3 ± 0.5 g/kg and 7.5 ± 0.5 g/kg of P, respectively.

The electrical conductivity of ashes undergoing lab-hardening treatments decreased rapidly, i.e. within a few days (see Paper **IV**). The electrical conductivity of MA-9c decreased from 1700 mS/m (untreated ash) to the rather stable 500 mS/m within the first week of hardening. In the case of FA-2b ash, electrical conductivity decreased from 3300 mS/m (untreated ash) to

the rather stable 1400 mS/m in about two weeks. A comparison between the composition of the leachates from fresh and hardened ashes suggested that the observed decrease in electrical conductivity levels was likely to be caused by the considerable reduction in Ca releases from hardened ashes, which was the element in solution which decreased the most (some differences in the release of K and Na were also observed, but only in the case of MA-9c leachates). It is worth mentioning that, because of the lower electrical conductivity levels (i.e. <2800 mS/m), hardened FA-2b ash can now be applied onto Danish forest soils at a higher ash dosage (3 tonnes/ha/10y) than the respective fresh FA-2b ashes (1 tonne/ha/10y).

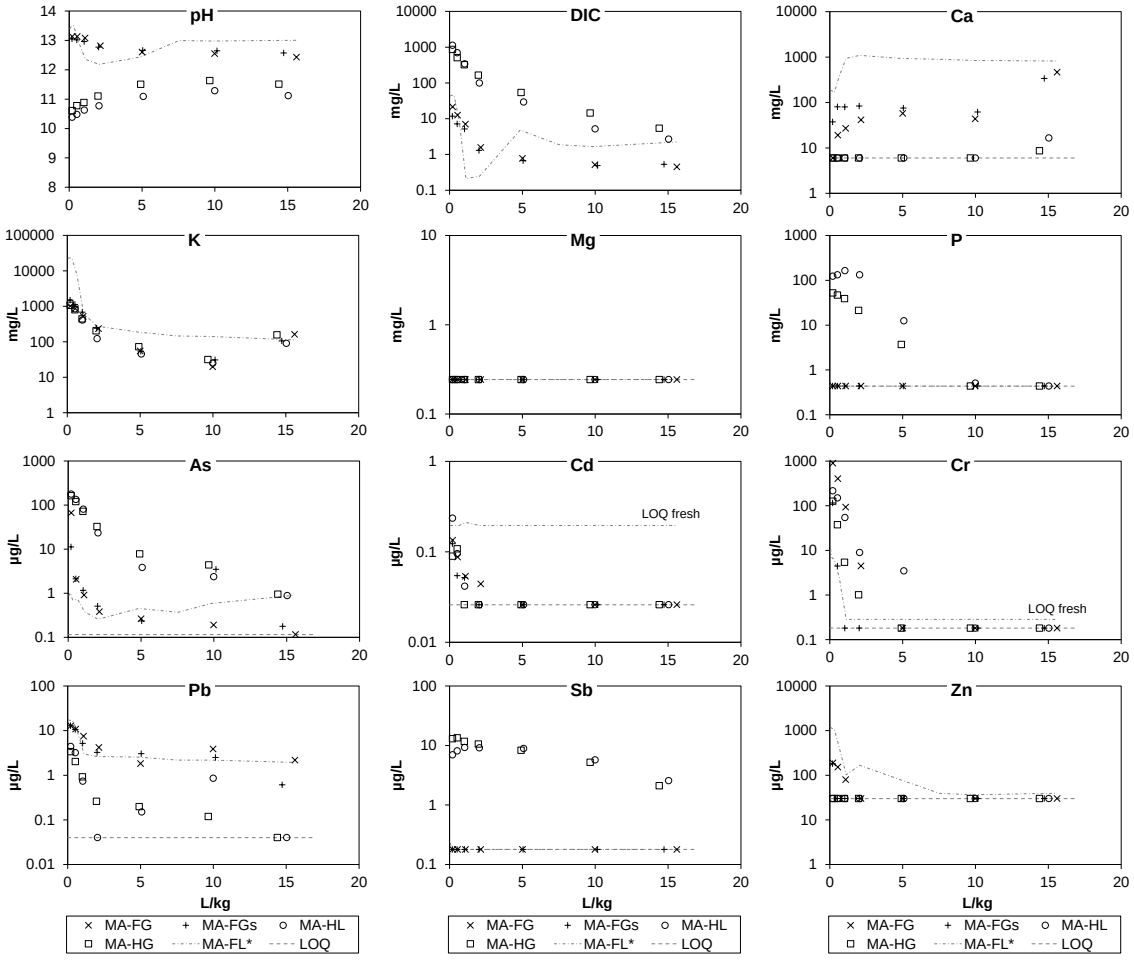

Figure 3. Concentration development of selected elements and pH in the leachates from pre-treated MA-9c ashes. DIC, Ca, K, Mg and P are expressed in mg/L; As, Cd, Cr, Pb, Sb and Zn are expressed in µg/L. [MA: indicates sample MA-9c; FG and FGs: granules made from fresh ashes with deionized water only and with addition of H_2SO_4, respectively; HL and HG: loose hardened ashes and granules from hardened ashes, respectively; FL*: fresh loose ashes; LOQ: limit of quantitation; LOQ fresh: LOQ of fresh ashes when higher than pre-treated ashes]. Adapted From Paper **IV**.

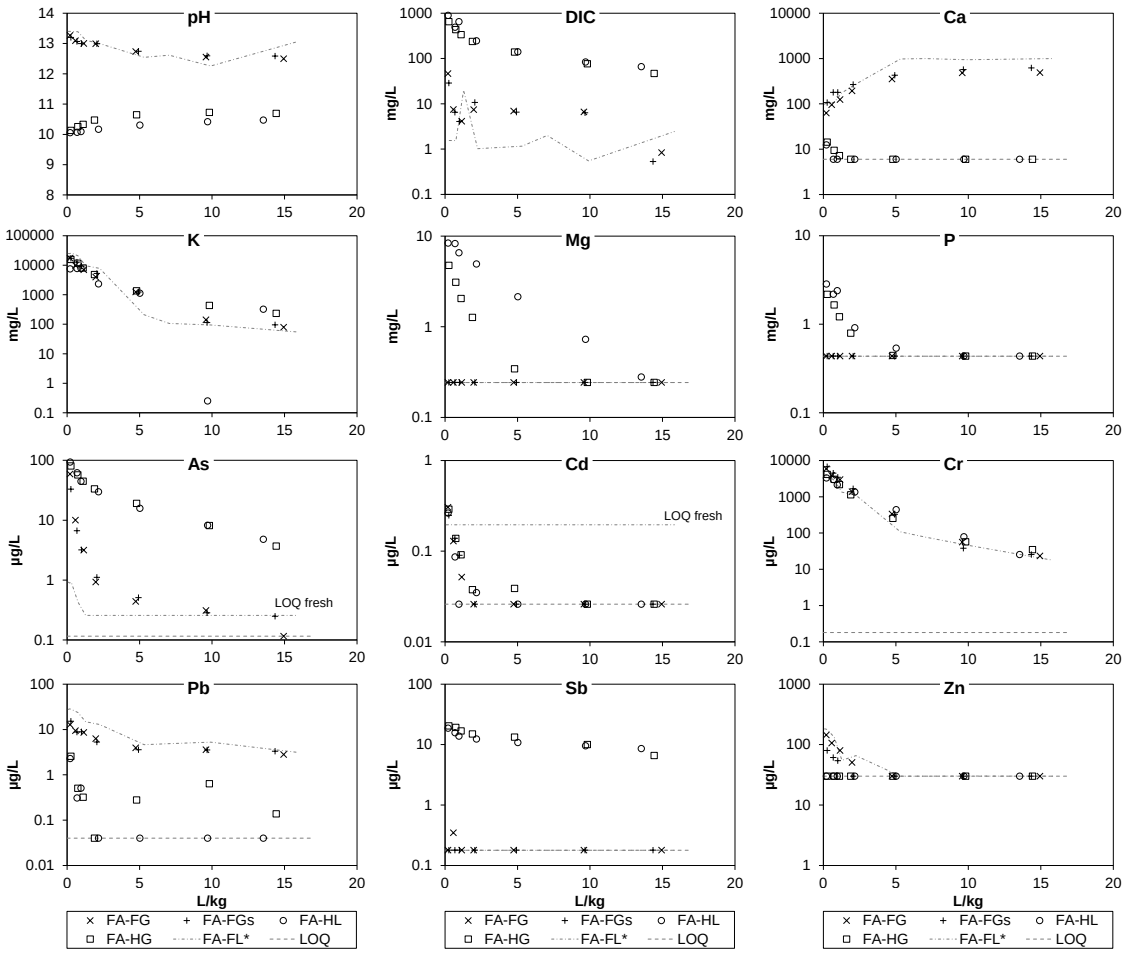

Figure 4. Concentration development of selected elements and pH in the leachates from pre-treated FA-9c ashes. DIC, Ca, K, Mg and P are expressed in mg/L; As, Cd, Cr, Pb, Sb and Zn are expressed in µg/L. [FA: indicates sample FA-2b; FG and FGs: granules made from fresh ashes with deionized water only and with addition of H_2SO_4, respectively; HL and HG: loose hardened ashes and granules from hardened ashes, respectively; FL*: fresh loose ashes; LOQ: limit of quantitation; LOQ fresh: LOQ of fresh ashes when higher than pre-treated ashes]. Adapted From Paper **IV**.

5 Wood ash utilisation on top of acidic nutrient-poor forest soil

Knowledge regarding the mobility of nutrients and contaminants through soil can be used as a basis for investigating impacts on soil in a wider context. While some studies have investigated the effects of wood ash application on percolating soil solutions (J. Eriksson, 1998; Gómez-Rey et al., 2012; Meiwes, 1995; Ozolinčius et al., 2005; Van Hees et al., 2003), further studies are needed in order to provide a more comprehensive understanding on the effects of using different wood ash dosages on diverse soil horizons, and on the potential migration of trace elements through the soil.

This section summarises the results of Paper **III**, in which wood ashes were applied onto two different soil horizons and the composition of the percolating soil solutions was monitored over time. Three different wood ash dosages were employed, and the short-/long-term release of nutrients, contaminants and alkalinity beyond the individual soil horizons was examined.

5.1 Soil leaching

The two soil horizons were strongly acidic (with a pH of about 4.2 for the O-horizon and 3.4 for the A-horizon) and their composition reflected the levels reported for other nutrient-poor Danish forest soils (Raulund-Rasmussen, 1993; Vesterdal and Raulund-Rasmussen, 1998). Each of the soil horizons (O-horizon and A-horizon) was packed into laboratory columns and investigated against three different wood ash dosages (3, 9 and 30 tonnes/ha) and one Ca-carbonate dosage (7 tonnes/ha), as described in Section 2.5. Water was pumped into the columns to investigate the percolating soil solutions. The soil columns were operated for about three months, corresponding to a cumulative water infiltration of ~2200 L/m^2 which, based on the site-specific soil infiltration rate of 270 ± 90 mm/year (Hansen et al., 2017), corresponded to about 8 years in the field. Figure 5 presents the composition of the percolating soil solutions from O-horizon for a few selected major and trace elements – more elements can be found in Paper **III**, as well as the figures for A-horizon columns.

Developments in the composition of the percolating soil solutions from the control columns were generally similar to those where the laboratory grade Ca-carbonate was applied, irrespective of the soil horizon – see Figure 5. The main exception was observed for As, which was mobilised from the O-horizon soil after adding Ca-carbonate. While the reason behind this mobilisation was unclear (possibly due to a displacement of As from the Ca^{2+} ions or to a change in the oxidation state from As(V) to As(III)), the observed concentration levels of As were relatively low, i.e. below the quality criteria defined for Danish groundwater (DEPA, 2015). These results suggest that the application of liming materials may have a very limited effect on the mobilisation of nutrients and contaminants from the soil columns.

Application of wood ash onto O-horizon and A-horizon increased the overall leaching concentrations of K, P and Si until the end of the column test (~2000 L/m^2), while a relatively short-term leaching of Cl, Mg and S (and K and Si, too) was also observed within the first 500 L/m^2 of infiltrating water (corresponding to less than two years in the field). Higher releases were generally observed for higher wood ash dosages, especially in the case of readily soluble compounds. In the literature, peaks in the concentration levels of readily soluble elements, such as K, Na, S (as SO_4^{2-}) and Cl have been commonly reported in percolating soil solutions after the application of wood ash (J. Eriksson, 1998; Gómez-Rey et al., 2012; Ludwig et al., 2002), whereas levels of extractable P and exchangeable Mg have generally been shown to increase in the soil and not necessarily in percolating soil solutions (Fransson et al., 1999; Gómez-Rey et al., 2012; Lundström et al., 2003; Saarsalmi et al., 2012). In the herein soil column experiment, irrespective of the soil horizon and the wood ash dosage, the observed concentration levels of Ca were generally lower than the column containing sand only, indicating that Ca was retained by the soil. In favour of this hypothesis, forest soil applications have generally reported increases in the soil exchangeable Ca levels (H. M. Eriksson, 1998; Gómez-Rey et al., 2012; Lundström et al., 2003); on the other hand, increases in the percolating Ca levels have also been commonly presented (see Augusto et al. (2008) and therein literature).

Wood ash application increased leaching concentrations of As and Cu, but only in the case of O-horizon columns. The leaching of Cu increased with the ash dosage, suggesting the occurrence of complexation reactions between the ash Cu and the soluble organic compounds in the soil (Augusto et al., 2008; Chirenje et al., 2002). The leaching of As reflected the trends and concentration levels reported by the Ca-carbonate treatment, indicating that

observed releases of As were most likely been mobilised from the soil (similarly to the case of Ca-carbonate application). Irrespective of the type of soil application, the composition of the percolating soil solutions was observed to be overall within Danish groundwater quality criteria (DEPA, 2015). Some exceptions were observed during the initial leaching of As, Cd, Cr and Pb from the A-horizon columns and the initial leaching of Cr and Pb from the O-horizon columns – for more details see Paper **III**. In general, however, similar concentration levels and trends were observed from all columns, even from the controls, indicating that the application of wood ash had a modest effect on the potential migration of trace elements beyond the O- and A-horizons. Overall similar observations, though limited to a very few trace elements (i.e. Cd, Cr, Cu, Pb and Zn), have been reported by Pitman (2006), who summarized the results of different field applications addressing the composition of the percolating soil solutions.

In general, adding wood ash and Ca-carbonate did not increase the pH of the percolating soil solutions compared to the controls. Similar observations were reported by J. Eriksson (1998) and Gómez-Rey et al. (2012) and it was concluded that the dissolved alkalinity was neutralised by the soil (as intended) and did not percolate beyond it. However, both soil horizons treated with the highest ash dosage indicated the so-called "salt effect" (e.g. H. M. Eriksson, 1998): relatively high amounts of salts being released from the ashes at the beginning of the experiment, favouring the displacement of exchangeable H^+, Al^{3+} and Mn^{2+} from the soil and a temporal pH decrease.

In the case of wood ash application, cumulative released amounts at 2000 L/m^2 showed that except for K, Na, P, S and As, all the other elements investigated in Paper **III** were released only up to a few percentage points. On one hand, this suggests that relatively high levels of nutrients such as K, Na, P and S may be available for local soil organisms. On the other hand, if relatively high ash dosages are being used, the low mobility of trace elements (e.g. Cd, Cr, Ni, Pb and Zn) should be evaluated for their potential accumulation within the specific forest soil.

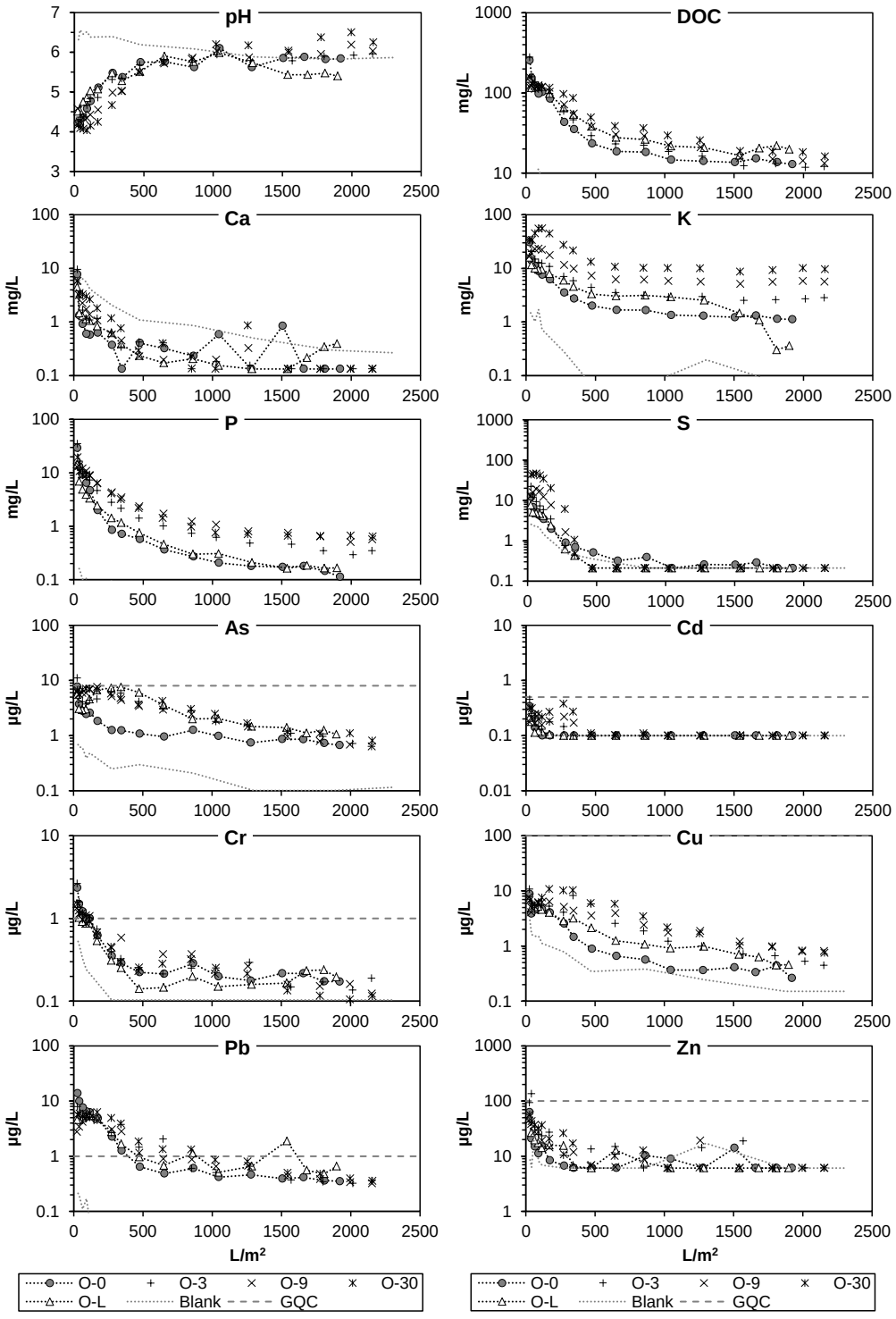

Figure 5. Composition of soil solutions percolating from the O-horizon columns after wood ash application (sample MA-9c). Concentration levels are expressed in mg/L for DOC, Ca, K, P and S and in µg/L for As, Cd, Cr, Cu, Pb and Zn [O-3, -9, -30: O-horizon columns subjected to wood ash application (3, 9 and 30 tonnes/ha, respectively); O-0: control; O-L O-horizon subjected to Ca-carbonate application; GWC: Danish ground water quality criteria (DEPA, 2015); blank: sand column]. Adapted from Paper **III**.

6 Conclusions

The analysis of the chemical composition of the Danish wood ashes demonstrated that 15 out of the 16 ashes complied with Danish ash quality criteria, indicating that these ashes may be applied onto forest soil. In general, the observed composition and leaching from these ashes were comparable with the overall levels reported in other investigations for similar combustion ashes. However, if the same ashes were landfilled, they would be classified as either “non-hazardous” or “hazardous” waste. Limits for non-hazardous waste were often exceeded by Cr and Se.

The use of extraction methods commonly employed to test the solubility of P from phosphatic fertilizers showed that relatively large amounts of P were dissolved from the investigated wood ash samples, both fresh and hardened: ~5.3 g/kg for the mixed ash sample (ash P content of 11 g/kg) and ~7.5 g/kg for the fly ash sample (ash P content of 21 g/kg). Based on these results, wood ashes appeared as a potentially valuable source of P if applied onto soil.

With regards to the geochemical model, mineral dissolution provided an acceptable description of the leaching processes most likely governing the release of major elements, such as Al, Ca, Mg, Ba, P, S, Si and Fe, during both pH-dependent and column leaching experiments. The inclusion of adsorption onto Al/Fe (hydr-)oxides and DOC-complexation provided an adequate description of the levels of trace elements (e.g. Cd, Cr, Cu and Zn) in the solution. Acidic conditions were observed to promote the solubility of not only potential plant nutrients such as P and Mg, but also trace metals like Cu, Cd and Zn. Leaching of Cl, Na and K was rather pH-independent; the primary release was observed at low L/S ratios. On the other hand, the release of Al, Ba, Ca, Cr, Mg, Sb, V and Zn was found to be distributed over a wider L/S interval, as indicated during column experiments, demonstrating that large underestimations of their released amounts would occur if estimates are made based on low L/S ratios. It was shown that differences of at least one order of magnitude were established between the cumulative releases at L/S 10 L/kg and at L/S 1000 L/kg.

Lab-hardening experiments indicated that relatively large changes in the mineralogical structure of the ashes took place within the first one to two weeks of hardening. In the case of full-scale hardening, some delay should be expected because of less optimal exposure to moisture and atmospheric

carbon dioxide. The acid neutralisation capacity of the ashes was practically not affected during the 11 weeks of lab-hardening, indicating only modest consequences for ash liming properties. Hardened ashes presented a lower equilibrium pH and considerably reduced levels of Ca leaching compared to fresh ashes. The leaching of Ba, Pb and Zn was also considerably reduced, whereas As, P, Sb, Si, V and Mg were enhanced. While hardening increased the short-term leaching of P from the ashes when in contact with water, the solubility of P in neutral ammonium citrate was not affected. Hardening was observed to be a relatively fast process, driven by the thermodynamic instability of the ashes. It is recommended to include hardening as part of ash management, irrespective of the final disposal route.

Granules made from fresh ashes provided a reduced leaching of mainly Ca, Ba, K and Na, where the magnitude of this effect appeared to depend on the specific surface area of the granules. Granules made from hardened ashes showed a leaching behaviour comparable to the loose hardened ashes. While the effects of granulation may be limited from a leaching perspective, the use of granules may however facilitate ash spreading through mechanical spreaders and minimise the generation of dust.

Applying wood ash onto acidic Danish forest soils promoted the migration of higher amounts of K, P and Si through the soil from a long-term perspective (until the end of the column experiment, i.e. ~2000 L/m^2); a relatively short-term leaching (until 500 L/m^2 of infiltrating water) of Cl, K, Mg and S was also observed. The magnitude of these effects was related to the application dosage. In general, despite the slightly higher levels of As and Cu migrating beyond the O-horizon soil after applying wood ash, the composition of the percolating soil solutions was generally within Danish groundwater quality criteria or comparable to the soil controls, indicating low mobility of the ash trace elements. The application of 30 tonnes/ha caused relatively large amounts of salts to dissolve from the ashes, which in turn induced the so-called “salt effect”, i.e. a temporary decrease in the pH of the percolating soil solutions. Conversely, the effects of using 3 and 9 tonnes/ha were overall comparable and limited (except for some differences in the released amounts of readily soluble elements), indicating that there may be some potential for increasing the currently allowed Danish ash dosages. Based on these experiments, the use of 30 tonnes/ha may not be recommendable.

7 Future perspective

Based on the knowledge and experience gained during this PhD work, some objectives for future activities are suggested.

- In order to promote the overall use of wood ashes, and to reduce the costs of spreading, future research and changes in the regulatory framework may wish to focus on slight modifications in wood ash application frequency and/or allowed dosage. For example, the cumulative ash dosage of 9 tonnes/ha over 75 years may be considered for application over two campaigns (e.g. 2 x 4.5 tonnes/ha) instead of three (3 x 3 tonnes/ha).
- The documentation of wood ash quality may consider including routine analyses of the neutralising value of the ashes. This information can be used by local institutions to document the liming properties of the applied wood ashes, as this parameter has been shown to vary largely across different wood ash samples
- Geochemical modelling may be used as a supporting tool to identify the type of interactions taking place between ashes and specific soils. A more detailed characterisation of site-specific soil parameters, however, would be needed (for example in terms of base saturation, organic matter composition, redox conditions and clay content) to adapt the model to site-specific conditions and more accurately evaluate the migration of trace elements through the investigated soil.
- Up-flow percolating conditions mimicking the application of wood ashes onto soil prevent the ashes from hardening. Further experiments could consider the use of actual soil cores with ash applied on top, in which case water could be sprinkled from the top and the analysis of the percolating soil water could be done at different depths.

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9 Papers

I Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties

II Long-term leaching of nutrients and contaminants from wood combustion ashes

III Recirculation of wood combustion ashes onto Danish forest soil: release of nutrients and heavy metals

IV Influence of wood ash pre-treatment on leaching behaviour, liming and fertiliser potential

TEXT FOR WWW-VERSION (without papers)

In this online version of the thesis, **papers I-IV** are not included but can be obtained from electronic article databases, e.g. via www.orbit.dtu.dk or on request from:

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